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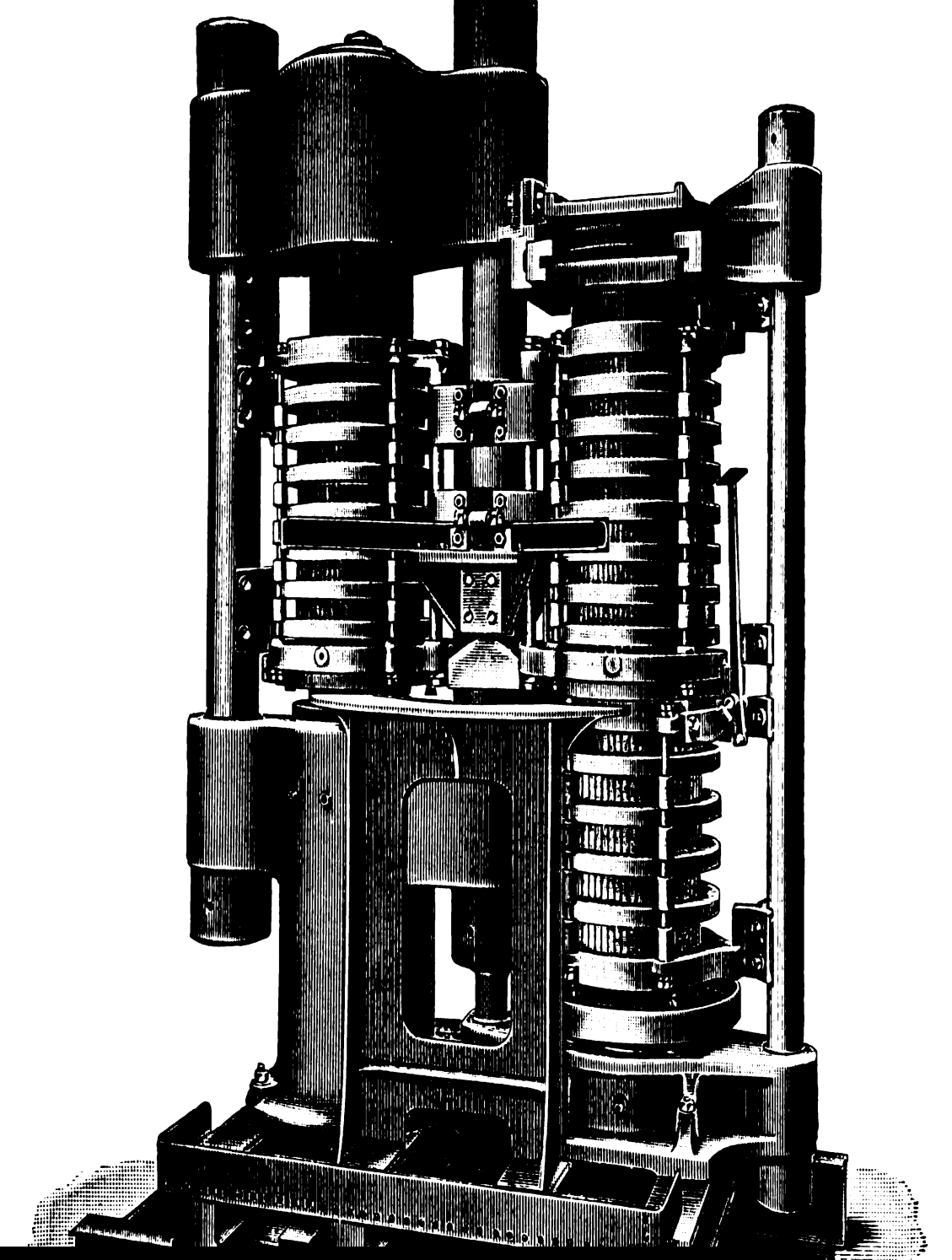

Cantor lectures on oils and fats

Julius Lewkowitsch, Royal Society of Arts (Great Britain)

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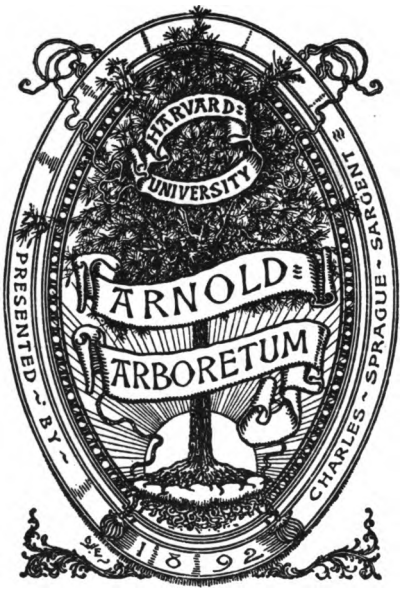

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SOCIETY FOR THE ENCOURAGEMENT OF ARTS, MANUFACTURES & COMMERCE.

Cantor Lectures

ON

OILS AND FATS: THEIR USES AND APPLICATIONS.

BY

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SYLLABUS.

LECTURE I.

Extent of the oil and fat industries—Sources of supply—Raw materials—Modern methods of manuacture.

LECTURE II.

Methods of refining—Bleaching—Demargarinating processes—The industry of edible oils and fats—Butter substitutes—Lard substitutes—Chocolate fats.

LECTURE III.

Burning oils—Paint oils—Lubricating oils—Blown oils—Boiled oils—Varnish industry—Linoleum industry—Vulcanised oils—Turkey red oils—Modern theory of hydrolysis of fats.

LECTURE IV.

Modern processes of saponification—Candle industry—Soap industry—Manufacture of glycerin—Recovery of glycerin from soap lyes.

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OILS AND FATS—THEIR USES AND APPLICATIONS.

LECTURE I.—DELIVERED JANUARY 25, 1904.

In its widest sense, our subject embraces not only those familiar products, oils and fats, or the products derived therefrom, with which everyone is acquainted, such as candles, soap, and glycerin, but it also includes some branches of the agricultural industries. For not only the cultivation of oleaginous seeds and the growing of oil-yielding fruits, but also the raising of fat stock fall within the purview of the industries which will occupy our attention in this lecture and the following ones.

Thus the oil and fat industries play a very important part in the domestic economy of our daily life, especially if we include amongst them, as indeed we must, the industry of edible oils and fats.

I do not intend to treat the subject from a historical point of view, and I will therefore plunge straightway into the present state of the industry. From the figures which will be found in the tables on the following pages it will be gathered that the industries with which I am dealing here belong to a branch of chemical industry which has found some of its highest developments in this country, and can favourably compare both in extent and scientific importance with that of any other country.

In order to give an approximate idea of the enormous sums that change hands in these industries in this country alone, I have compiled from the Board of Trade returns the figures contained in the following four tables (pp. 6, 7).

SOURCES OF SUPPLY.

Fatty oils and fats occur in every part of the vegetable and animal organisms. They accumulate, however, in certain parts of the plant or animal in greater quantities than in others. In plants, they are generally contained in some considerable quantities in the fruits or seeds, so that their extraction becomes commercially feasible.

We are able to produce fatty oils and fats synthetically from fatty acids and glycerin, and it may become possible in the distant future to manufacture the fatty acids themselves from petroleum hydrocarbons. Nature, however, has so bountifully supplied us with the raw material, that the production of oils and fats by synthetical methods will for a long time to come lie outside the domain of practical considerations.

As the supply of home grown oleaginous seeds is altogether a negligible one, and furthermore, as the quantities of home produced fats such as lard, tallow, butter, play an insignificant part as compared with the total quantities that are brought into the market, foreign sources of supply forced themselves at an early stage of our industries on the attention of the manufacturer.

Owing to the geographical position of this country, it is no wonder that the earliest works which were erected inland, rapidly migrated to the seaports of London, Liverpool, Hull, Bristol, Glasgow, and Leith. These towns thus became the great emporia of the fat and oil trade in this country. Here we receive the enormous quantities of oleaginous seeds: the linseed from India, from the Argentine, from Russia, and from Canada, to be converted into linseed oil for the soap and paint and allied industries, and into linseed cake for our cattle-raising counties. Here is landed the cotton seed that flows into this country

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TABLE I.—IMPORTS.

	1898.	1899.	1900.	1901.	1902.
	£	£	£	£	£
Butter	15,961,783	17,213,516	17,450,435	19,297,396	20,526,690
Margarine	2,384,381	2,549,476	2,464,825	2,556,679	2,569,503
Cacao Butter	29,559	28,461	80,162	40,792	10,948
Oleomargarine	257,595	263,435	300,253	298,810	292,988
Lard	2,887,801	3,068,975	3,266,582	4,037,689	4,118,992
Imitation Lard	89,025	90,010	98,629	154,239	284,830
Oils—					
Fish, Train or Blubber	323,194	332,703	389,712	453,809	473,218
Sperm	26,154	14,293			
Animal	62,704	74,531	117,131	120,427	93,438
Castor	172,091	156,571	78,847	155,581	160,421
Cocoanut	344,108	545,642	667,204	594,154	719,357
Olive	608,122	553,286	461,084	581,893	657,956
Palm	975,427	1,037,265	1,086,555	1,370,645	1,679,610
Seed	689,934	879,171	1,038,564	1,193,577	913,642
Oil Cake—					
Linseed	1,465,730	1,589,802	1,395,916	1,272,144	1,255,066
Cottonseed	765,799	987,445	1,051,528	1,036,309	1,103,881
Other sorts	52,715	71,997	100,097	105,193	113,991
Seeds—					
Cotton	2,069,111	2,036,550	2,624,450	2,705,597	3,285,650
Linseed	2,920,634	3,383,962	4,162,146	4,263,931	4,486,997
Rape	367,736	307,053	246,620	298,426	385,708
Other Seeds	339,609	355,352	387,138	546,132	539,159
Tallow and Stearine	2,066,433	2,380,033	2,835,217	2,333,246	2,708,717
Candles	27,740	21,822	23,182	21,347	17,921
Soap and Soap Powder	..	..	244,345	315,026	428,850
Soap (transparent)	774	604	511	538	450
Linoleum	..	..	119,661	73,482	70,946
Varnish	45,655	47,001	56,397	47,637	54,213
	33,973,814	37,689,116	40,929,185	43,874,659	46,953,142

TABLE II.—EXPORTS.

	1898.	1899.	1900.	1901.	1902.
	£	£	£	£	£
Butter	59,731	53,195	55,792	59,376	79,130
Margarine and all artificial Butters	16,434	7,586	7,111	10,057	11,347
Oleomargarine	21,954	26,874	16,803	16,857	31,283
Oils:—					
Linseed	377,307	476,110	588,866	661,448	655,082
Cottonseed	323,191	217,890	428,404	386,407	660,695
Other Seed Oils	67,645	64,657	98,014	109,813	114,116
Oil Cake	?	?	200,336*	237,162*	145,523
Grease, Tallow, and Animal Fats	759,516	850,892	758,563	820,778	778,336
Candles†	329,167	412,181	338,138	432,714	433,549
Soap	829,610	941,575	939,510	999,524	1,126,102
Oil and Floorcloth	1,000,447	1,164,267	1,312,833	1,298,007	1,465,845
	3,785,002	4,215,227	4,804,370	5,032,143	5,501,008

* These figures include sweetened food.

† Contain paraffin.

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TABLE III.—Re-Exports.

	1898.	1899.	1900.	1901.	1902.
	£	£	£	£	£
Butter	319,806	257,999	258,934	254,746	227,576
Margarine and all artificial Butters	24,721	33,319	27,882	35,937	46,249
Cacao Butter	5,645	276	792	1,072	926
Oleomargarine	56,410	53,076	87,834	83,438	60,566
Lard	674,828	810,903	480,797	551,512	155,457
Imitation Lard	11,875	4,332	2,276	1,453	6,548
Oils—					
Fish, Train, Blubber, Sperm	30,426	24,726	33,335	34,844	33,865
Animal	14,127	9,024	5,743	4,945	3,388
Castor	21,529	17,474	16,995	16,733	16,586
Cocoanut	80,337	134,402	176,952	201,986	219,183
Olive	124,728	154,773	81,110	109,915	143,759
Palm	623,664	657,796	721,397	762,427	866,163
Seed	83,746	59,361	59,119	74,566	77,254
Oil Cake—					
Linseed	3,582	1,713	1,649	595	1,092
Cotton seed	104	169	174	1,240	281
Other sorts	26,695	23,147	22,497	18,584	16,753
Seeds—					
Cotton	329	1,909	6,212	779	2,468
Linseed	245,597	166,586	343,031	410,694	396,044
Rape	44,326	48,040	45,581	31,783	70,279
Other sorts	220,892	189,766	211,989	324,677	303,656
Tallow and Stearine	1,065,143	1,165,687	1,232,649	324,677	303,656
Candles	13,711	9,759	15,982	14,082	6,752
Soap and Soap Powder	..	..	18,434	17,194	18,683
Soap (transparent)	234	87	45	63	54
Floorcloth	..	..	7,308	6,848	6,239
Varnish*	1,363	2,739	2,415	462	1,115
	3,693,828	3,827,063	3,861,132	3,285,252	2,984,592

Most of Varnishes are included under "Paints."

TABLE IV.—Summary.

	1898.	1899.	1900.	1901.	1902.
	£	£	£	£	£
Imports	33,973,814	37,689,116	40,929,185	43,874,659	46,953,142
Exports	3,785,002	4,215,227	4,804,370	5,032,143	5,501,008
	37,758,816	41,904,343	45,733,355	48,906,802	52,454,150
Less re-exports	3,693,828	3,827,063	3,861,132	3,285,252	2,984,592
	34,064,988	38,077,280	41,872,223	45,621,550	49,469,558
Add home products—					
Butter (estimated)	..	..	3,500,000	..	3,850,000
Lard (estimated)	..	..	1,000,000	..	1,100,000
Tallow (estimated)	..	..	3,000,000	..	3,300,000
	..	..	49,372,223	..	57,719,558

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from Egypt, and more recently from Bombay and the Levant, to yield edible cotton seed oil, soapmaking oil, and cotton seed cake. Here also is imported the rape seed from India, the castor seed, and in smaller quantities some other seeds, that have helped to create the vast seed-crushing industry which has reached, through the inventions of two Englishmen, Bramah and Armstrong, a completeness of mechanical detail which has maintained the supremacy of our country in this industry.

Enormous as are the quantities that are thus imported and worked up in this country, still they represent only a small quantity of the oleaginous seeds that nature offers us. Thus, India, China, and Japan possess vast stores of seeds, yielding safflower oil, bean oil, tung oil (Japanese or Chinese wood oil), and other oils, which are awaiting industrial application. All that appears to be required is better communication to stimulate the cultivation of oleaginous seeds.

Vaster still are the stores of hard vegetable fats which tropical countries such as India, the Sunda Islands, South America, and tropical Africa are able to furnish. Hitherto only two or three kinds of vegetable fats have found extensive use in this country, namely, cocoanut oil and the two oils obtained from the palm tree—palm oil and palm kernel oil. Smaller quantities only of other fats, such as Mowrah seed oil and Mahwah butter, reach this country, whereas the Continent of Europe seems to be less conservative in the choice of its raw materials. Thus, Chinese vegetable tallow and shea butter are chiefly worked up in Marseilles and in the North of Europe, whereas only comparatively small quantities reach this country. The vast stores which the Malayan Archipelago alone could furnish seem to be practically unknown to the majority of manufacturers.

This is not the place to examine whether this feature is due to the want of communication in India, or to the want of enterprise and the indolence of the natives. In the case of palm oil, at least, which could certainly be employed in much larger quantities, it is owing to the deadly climate and to the laziness of the negro that one of the most admirable raw materials of our staple industries cannot be obtained at a price which should be much lower than that at which it is supplied at present.

Nor does it appear that those who are most interested in the shipping trade of the West Coast of Africa take such steps as are required to foster this industry. We would do well to imitate the example of Germany who, since she entered into the possession of colonies on the West Coast of Africa, has taken the most energetic interest in promoting the cultivation of the palm tree, which yields one of the chief exports of the Guinea Coast. We may confidently expect that our Imperial Institute will, like similar institutions in France, Germany, and Holland, help in arousing the interest of the manufacturer, and place before him the treasures that are still lying unused in our Colonies.

[Here a large collection of oil and fat-yielding seeds was shown. Most of the Indian specimens had been contributed by the Imperial Institute through the kindness of Prof. Dunstan.]

With respect to the marine animal oils, it is but natural that they should be produced in this country on a very extensive scale. The industry of medicinal cod oil is naturally small in extent, whereas the industry of commercial cod oil and fish oils has received an enormous impetus during recent years, through the replacement of the old sailing craft, which had to keep out at sea for some days before a sufficient amount of livers were collected, by fast steamers which bring in their nettings within one day.

Thus we obtain large quantities of oil; and yet these do not seem to suffice, for very considerable quantities of cod oil are imported from Newfoundland, as also fish oil from Japan. The large representative collection of seal, whale, and allied oils which I place before you will give an idea as to the extent this branch of the oil industry occupies in this country.

Turning to the solid fats of the animal kingdom, the production of lard, of tallow, and of butter in this country is but an insignificant one as compared with the quantities we import. The changes in the source of supply that have occurred during the last 20 years do not appear to be well-known. The name of "Petersburg yellow candle tallow," once a household word with the tallow chandler and soapmaker, has passed into the limbo of things that were. Russia, instead of exporting tallow, has become a large importer of Australian tallow. Up till a few years ago, the United States of America have been supplying this market with a large amount of its requirements; but it seems as if America will in a few years drop out of the rank of those countries which can spare any supplies for us.

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ustralia and New Zealand, in conjunction ith the Argentine, are now our chief sources f supply of this indispensable raw material r our industries. The high prices that were ie result of the long-lasting drought in Aus-alia are bound to stimulate an increased pro-uction, and it may be hoped that under the eneficent rule that has recently gained its pre-ominance in South Africa, the Transvaal and)range Colony will become great cattle-aising centres.

Owing to the large consumption of meat in his country, the amount of "home tallow" home-rendered tallow) is very considerable. t seems, however, impossible to state even ipproximately the amount so produced, as the nost experienced dealers are at a loss to know .t what figure to place the home production.

From the first table given above may be gathered the enormous amount of butter that s imported into this country. Not only are Holland, Denmark, and Sweden competitors n this market, but even Siberia and Australia iave entered the lists, and it must be expected hat, under the stimulus of the expanding consumption, improvements in cold storage nethods will permit the products of the An-ipodes to reach us in the same state of fresh-ess as they arrive from neighbouring countries.

A few words only can be said about lard. It s well known that our chief supplies come rom the United States, where as many as o,ooo hogs are killed per day in some of the normous packing houses, and worked up on he same day into all the products that can be btained from them. Owing to the desire on the art of the manufacturer to produce the largest ossible quantity of lard, the word "lard" has eased to have its old meaning, *i.e.*, "fat from he leaf," and in the majority of cases it must e understood to mean the fat that is derived om any part or all parts of the hog.

The methods of producing fatty oils date ack to the remotest times in the history of ankind. It is therefore obvious that the echnical appliances used even at the present ay range from the simplest contrivances con-tructed by the natives of Asia and Africa up to ie most elaborate machinery employed in this ountry.

Time does not permit me to present here the evelopment of this industry from the early awn of civilisation, and I must content myself ith contrasting by means of a few slides shown on the screen) the present-day manufac-ire of palm oil in West Africa and the Philip-pines, and of the Chinese bean oil in Manchuria, with the methods in vogue in this country.

The modern processes divide themselves naturally into two classes,

I. Recovery of oils by expression.

II. Recovery of oils by extraction with volatile solvents.

Common to both processes is the machinery required for the preliminary treatment of the fruit or seeds.

I. Recovery of Oils by Expression.

The recovery of oils by expression has reached the very complete system in vogue nowadays in the best equipped establishments through the invention of the hydraulic press and of the accumulator, to which reference has been made already.

Since the machinery required for the preliminary treatment of the fruit or seeds must vary with each particular kind of fruit or seed, the preparatory operations for laying bare the fat-containing cells of, *e.g.*, cocoanuts, will naturally differ from those necessary in the case of linseed. I will therefore illustrate, by means of a series of lantern slides, the preliminary treatment of a few kinds of fruits and seeds, such as palm kernels, copra (dried cocoanut kernels), arachis nuts, castor seeds, cotton seed, linseed, and safflower seed.

[The following lantern slides were shown:—Screen and magnetic separator for palm kernels and copra; palm kernel and copra breaking mills, breaking rollers for copra, arachis nut decorticator, separator for decorticated arachis nuts, decorticator for castor seed, cotton seed delinting machine, cotton seed decorticators (different types; American and English machines), linseed screen, and plants illustrating the working of the various machines described. Samples of the different seeds and various kinds thereof (especially various kinds of linseed and cotton seed) were also shown.]

The immense quantities in which smaller seeds such as cotton seed or linseed are crushed, necessitated the construction of special warehouses or silos, where the seeds are stored in a similar manner as grain is warehoused, the seed being frequently turned so as not to heat spontaneously, since heating acts detrimentally on the quality of the oil.

The seed entering the oil mill from the silos is reduced to "meal" on passing through crushing machinery of the kind I show in the lantern slide representing the Anglo-American five-roller machine. The comminuted seed is either expressed in this state

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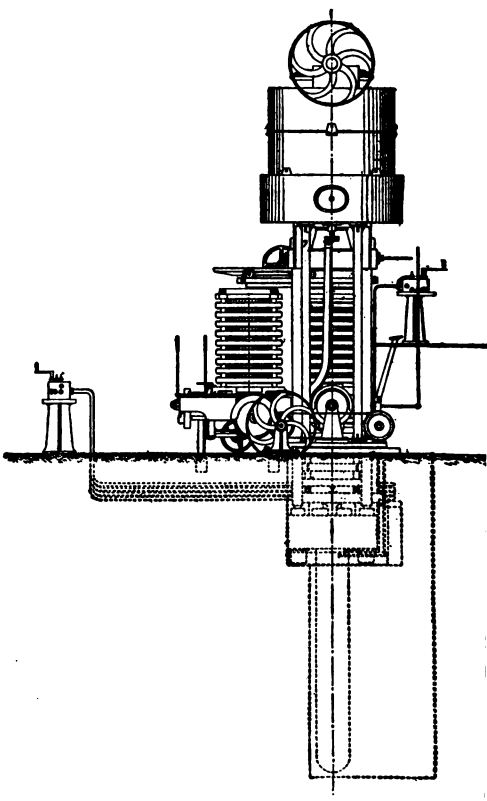
(production of oils for edible purposes), or conveyed by means of an elevator into a kettle in which the seed is warmed (production of oils for manufacturing purposes) by means of steam, which causes the cells to burst rapidly, renders the oil more fluid, and perhaps also helps to coagulate some albuminoid matter, all these operations combining to facilitate the subsequent moulding of the meal into cakes.

On opening a slide, an exactly-measured quantity of heated seed then falls out, and drops into a measuring-box. On being drawn forward, this allows the seed to fall on to a press-cloth of the desired shape of the oil-cake. By a preliminary pressing sufficient consistence is given to the cake so that it can be carried, wrapped in the cloth, to the hydraulic press. This consists, in the Anglo-American system of seed-crushing, of an open press, fitted with about 16 iron press plates, between which the cakes are inserted by workmen. The press is packed with cakes until full; the ram is then driven up by machinery, at first with the help of an accumulator, and finally by hydraulic pumps. The oil exudes from the meal, drains off, and is collected in tanks below the press or set of presses which are generally arranged in the Anglo-American system in a battery of four presses. After releasing the pressure the cakes are taken out, and the edges, which are soft and oily, are trimmed off in a cake-paring machine. Obviously, the cakes retain a certain quantity of oil, and in the case of those seeds which contain a large amount of oil, such as castor seed, a second expression is required.

The hard cakes are, therefore, broken up in a cake-breaking machine, whilst the softer cake-parings are triturated in a special machine. In some cases an edge-runner mill is used for the same purpose. (All the machines mentioned, as also an *ensemble* of an oil mill plant, were shown in lantern slides.)

The first expression of seeds that are rich in oil, such as those containing more than 40 per cent., leads to some difficulties in the open hydraulic press, since the oily meal causes "spueing," *i.e.*, the soft mass is apt to exude through the cloth. Hence, in modern installations, seeds of this kind are frequently expressed in a "clodding press," *i.e.* a hydraulic press provided with a circular box or cage into which the material is filled. The box is either constructed of metal staves (vertical steel bars), held together by a number of steel rings, or consists of a cylinder having a large number of perforations. These presses, genera worked in sets of two, or three, or mo have a seed kettle fixed on the top of t press (see Figs. 1, 2); the kettle is provid with an opening or openings, corresponding the chamber or chambers in the heads of t press or presses. These chambers can closed at the top and bottom by slide actuated by levers, and are designed to co tain so much meal as is required to form o cake. The measured charge of meal is th

FIG. 1.



allowed to fall into the press box, and covere with a circular metal plate. This operation repeated until the press is full, when hydraul pressure is applied, and a ram forces the bo against the sliding block at the head of th press. The oil exudes, and the meal, presse into circular cakes, is ready for the secon expression. After releasing the pressure an removing the sliding block, the cakes a forced out by the hydraulic ram. They a then broken into meal, and subjected to second expression in the Anglo-American h draulic press, described already.

Modern improvements in the mechanic part of the process dispense even for th

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FIG. 2.

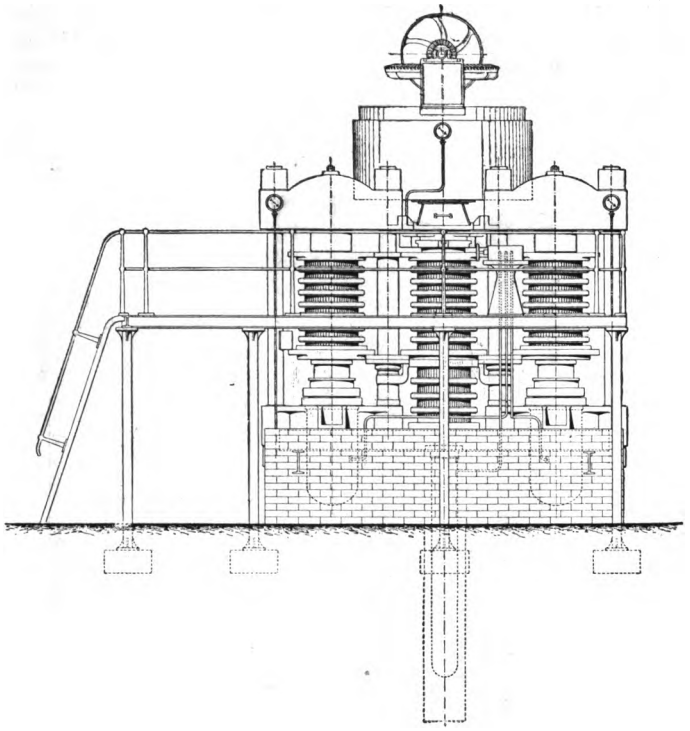
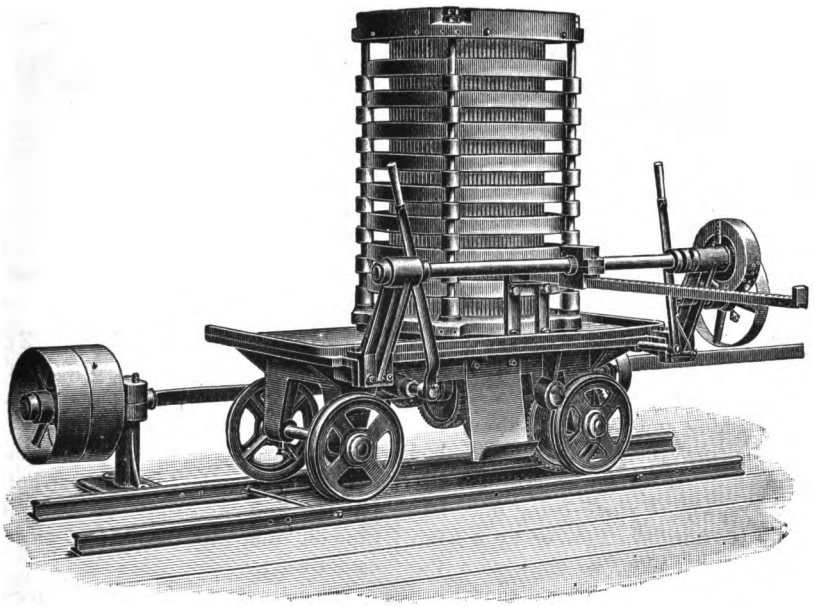


FIG. 3.



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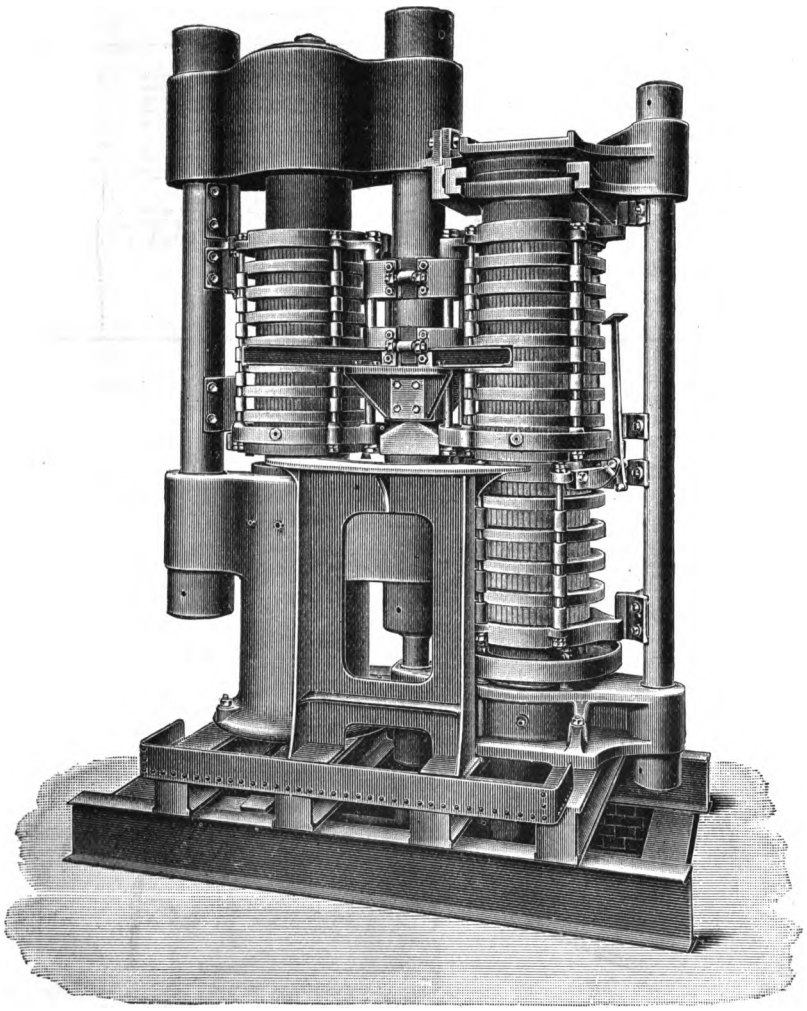
second expression with the open Anglo-American press. The finishing presses are of the same type as the press in which the first expression is carried out, and by making the press cages removable, the pressing operation can be made a practically continuous one. These press cages can either be transported by means of a power-driven carriage (Fig. 3) to the finishing presses, or if one preliminary press is combined with one or two finishing presses to a battery, the cages can be conveyed into the adjoining finishing press by a swinging arrangement (Fig. 4, and Fig. 5), its place being filled immediately by a charged cage, or by a cage containing finished cakes, so that, with the exception of the time required for withdrawing the pressing cages and replacing them, th work goes on continuously. Further advantage are offered by these presses, in that the cake require no paring, and that great saving c press cloths is effected in comparison with th open plate process of the Anglo-America system.

FIG. 4.



II. RECOVERY OF THE OILS BY EXTRACTIO WITH VOLATILE SOLVENTS.

The second class of processes for obtainin oils and fats from fruits or seeds is represente by the so-called "extracting processes," and i very largely employed in the extraction of oliv oil marc and palm kernel oil from palm kernel rape oil from rape seed, and castor oil fro castor seed.

The solvents employed on a large scale a

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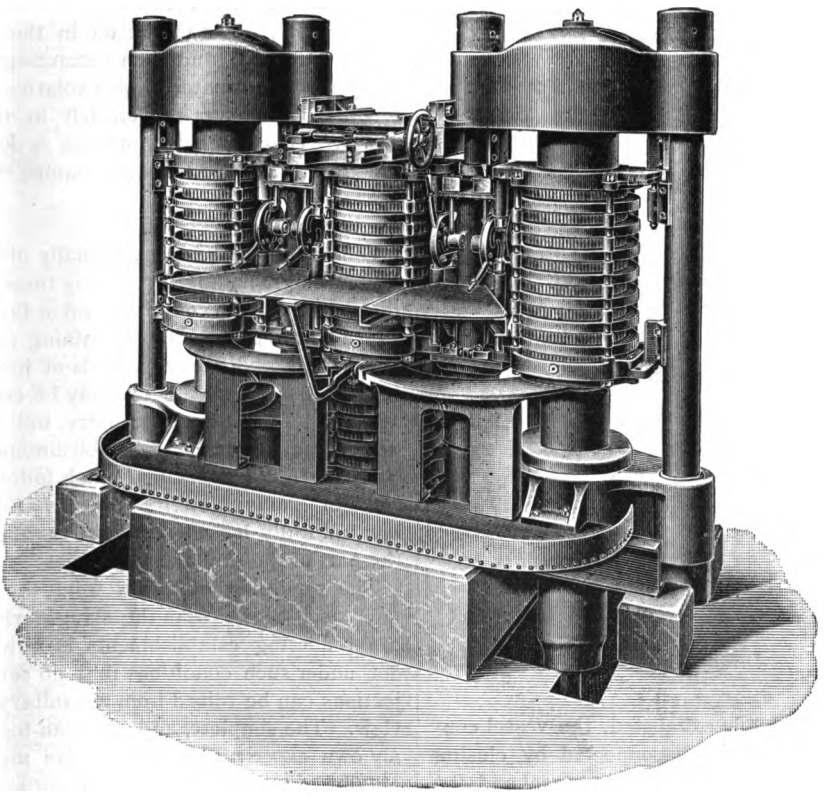
almost exclusively petroleum ether and carbon bisulphide ; ordinary ether must be considered as altogether outside the range of the solvents used on a large scale owing to the considerable loss of solvent involved, and furthermore on account of the great danger of fire. The same danger attaches, although in a somewhat minor degree, to the employment of petroleum ether. More diminished still is the danger of an inflagration in the case of carbon bisulphide ; as this solvent is heavier than water, the vapours are less liable to come in contact with an open flame. Hence, carbon bisulphide is largely employed for the extraction of oil, notably for the extraction of the marc of olives. Still, owing to the physiological effect this solvent has upon the workmen, coupled with the danger caused by the action of impure carbon bisulphide on iron, which has frequently led to conflagrations, the employment of carbon bisulphide is restricted.

An ideal solvent would be carbon tetrachloride, which is non-inflammable, and has the further advantage of being heavier than water. Its high price has, however, hitherto prevented its technical application. Furthermore, its physiological effect (similar to that of chloroform) on the workmen would seem to prevent its general application.

The type of apparatus employed on a large scale depends on the temperature at which the extraction is carried out. In the case of cold extraction (preferable as regards fire insurance), the seed is placed in a series of closed vessels through which the solvent percolates on the counter-current system. The battery of vessels is so arranged that any one vessel can be made the last of the series, ready to discharge the extracted meal, and to be refilled with fresh meal, so that, with the exception of the time required for charging and discharging, the process is practically a continuous one. The solution of extracted oil or fat is then transferred to a steam-heated still, where the solvent is driven off, and recovered by condensing the vapours in a cooling coil. Thus the same quantity of solvent is used over and over again. The last traces of volatile solvent in the oil or fat are driven off by a current of open steam which

FIG. 5.



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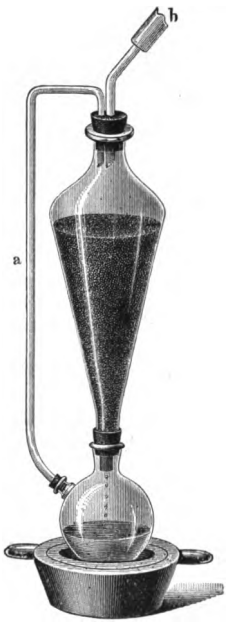
is blown through the oil or fat whilst kept hot.

The extracting processes in the hot are carried out in apparatus, the principle of which is illustrated by Fig. 6 (where the condenser is not shown). I further show, in a few lantern slides, several types of apparatus used on the large scale.

The principle involved in more elaborate forms of plant employed on a large scale is exemplified by the well-known Soxhlet extractor. The extraction here takes place continuously, with a limited amount of solvent charged once for all into the apparatus. When the seed is

FIG. 6.



deemed completely exhausted, the vessel containing the seed is disconnected by closing taps between the oil containing vessel and the condenser, so that the volatile solvent can be immediately distilled off and and condensed, whilst the seed-containing vessel is freed from the last traces of volatile solvent by open steam, and emptied and recharged with fresh seed. More compact still are extractors illustrated by that form of laboratory apparatus in which the meal-containing vessel is placed inside the flask charged with the solvent. Thus, in some form of extractors, a basket containing the crushed seed is placed on a support at some height above the bottom of the vessel charged with the solvent, so that, on heating, the vapours of the solvent pass through and round the seed, whilst that portion which leaves the vessel in form of vapour is condensed in a separate condenser, from which the liquefied solvent falls back and percolates the seed. Finally, when the meal is exhausted, the solvent is driven off, and the condensed solvent collected in a separate vessel.

[All these types of apparatus were illustrated by means of lantern slides; finally a series of slides were exhibited, showing a large rape oil extracting plant.]

In special cases, notably so in the case of olive oil, a combination of the two processes described under the headings I. and II. commends itself. The combined method consists in expressing most of the oil in the cold (for edible purposes), and then extracting the partially expressed material with volatile solvents, in order to recover the oil left in the press cakes. This combined process is known on the Continent under the name "huilerie mixte."

Animal oils and fats are usually obtained in a very simple manner by heating those parts of the animals which contain the oil or fat, so as to cause bursting of the fat-containing cells. The older rough and ready methods of heating the adipose tissue over free fire may be considered as almost extinct in this country, but it is still being practised in small establishments on the Continent. The nuisance which follows in the wake of a manufacturing process of this kind has naturally led to stringent regulations on the part of the sanitary authorities.

The rendering of tallow from the "rough fat," as it comes from the slaughterhouses to the rendering establishments is now carried out under such conditions that no serious objections can be raised from a sanitary point of view. The simplest, and as I can testify from my own experience, very effective method for obtaining tallow for technical purposes, is to throw the rough fat into covered lead-lined vessels provided with steam coils, outlet taps, a trap door for charging the rough fat, and a wide outlet through which any offensive vapours that may be given off are conducted through closed pipes to the chimney stack, or boiler, or fire grate. Hot water is then run on to the fat, and the steam turned on. After heating for a sufficient length of time the steam is shut off, when the clear melted fat rises to the top. It can then be drawn off ready for use, or into another vessel for further purification (refining, bleaching). The animal tissue, &c., still containing considerable quantities of fat, is boiled

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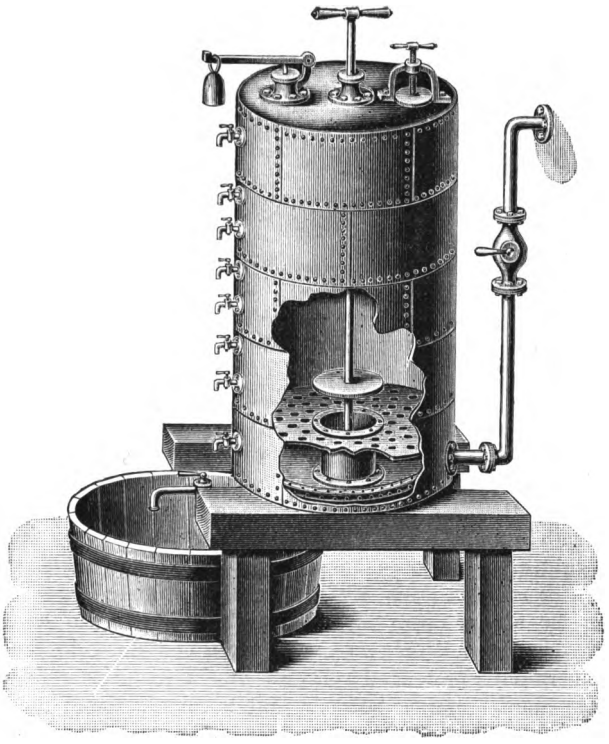
up again with steam, after a few per cent. of dilute sulphuric acid have been added, whereby the cell membranes are "cut," so that they part more readily with the remainder of the occluded fat.

Since in the older method of melting the rough fat over free fire, fat would not infrequently burn on to the sides of the vessel, or even boil over and run into the flue, whereby volumes of the pungent acroleïn were sent into the atmosphere, a number of apparatus have been designed in which the tallow is melted in closed vessels under pressure. Such vessels—termed digesters—consist essentially of a vertical boiler provided with a false perforated bottom, and constructed to withstand a pressure of several atmospheres. Live steam is turned into the boiler below the perforated bottom on which the rough fat rests. At the elevated temperature the mass parts readily with its occluded fat, and in a shorter time than by steaming at the ordinary pressure. The first apparatus of this kind was designed by Wilson (Fig. 7); it has served as a prototype for a number of more or less complicated digesters now in use.

FIG. 7.



The rendering of lard in the large packing-houses in the United States is carried out on similar lines. More primitive are the methods for obtaining liver and blubber oils.

(The manufacture of the last class of oils was then illustrated by a very complete series of samples, of seal oils, whale oils (No. 0, 1, 2, 3, 4), sperm oils, and bottlenose oils.)

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Lecture II.—Delivered February 1, 1904.

We have seen in the last lecture how the raw oils and fats are prepared by modern methods.

The oils and fats thus obtained are in their fresh state practically neutral. If care be exercised in the process of rendering animal oils and fats, the fatty matter is very often sufficiently pure to be immediately worked up in those industries to which they serve as raw materials. If, however, they are allowed to remain in contact with animal tissue, they are liable to very rapid deterioration. Thus, freshly rendered lard or suet, or even whale oil, will keep sweet for a very long time if protected from light, air, and moisture, whereas the same materials through prolonged contact with putrescible animal matter become dark in colour, and rich in free fatty acids. This is especially exemplified by the five samples of whale oil shown here. Of these, whale oil "No. 0," is perfectly sweet and water white, whereas the lower grades passing through whale oil "No. 1" to "No. 4," become gradually darker, and finally acquire an offensive odour, in consequence of having remained in contact with the flesh and bones for a somewhat prolonged time.

The vegetable oils obtained by expression contain frequently mucilaginous matter and other impurities, such as vegetable fibres, which pass through the press cloths. There are also admixed with the oils traces of moisture, which render them somewhat turbid, dark, and unfit for immediate use; not only for the table, but also for manufacturing purposes. Formerly these impurities were removed from edible oils, such as olive oil, by the simple method of allowing the oils to rest for some length of time, when the moisture and the mucilaginous matter, &c., would settle out. This crude process is no longer employed in large establishments, the clarifying of the oils being much shortened by filtering through a filter press, or brightening by blowing with air.

Other crude oils require more elaborate purification (refining) before they are placed on the market. Notable examples of this kind are cotton seed oil and rape oil. The sample of Egyptian crude cotton seed oil I show here has been expressed direct from the crushed seed. It ranges from a ruby red to almost black colour, due to the dark brown colouring matter contained in the cells of the cotton seed. The oil is refined by treatment with dilute caustic soda; the latter combines with the colouring matter and the free fatty acids in the oil and forms a precipitate which falls down on standing, leaving the oil clear and bright. This crude rape oil, again, is refined by treatment with concentrated sulphuric acid, and yields the refined oils shown here. From these two examples, which can be multiplied by the series of other oils which you have before you, both in the crude and refined state (linseed, castor, fish, sperm oils, and various rape oils, &c.), it may be gathered that the processes adopted on a manufacturing scale vary greatly with the nature of each individual oil or fat.

The methods of bleaching or decolourising oils also vary with each kind of oil or fat. Time permits only of a brief glance at the methods employed on a large scale.

Bleaching by sunlight, one of the oldest processes, is naturally only feasible on a small scale, as the length of time and the space required to expose as large a surface as

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possible must naturally be costly. Still, in some cases, as in the bleaching of beeswax or in the bleaching of linseed oil for artists' use, this method is being practised. Since the fatty matter undergoes practically no change, the products do not suffer as much as they would in the chemical processes of bleaching.

Bleaching by the aid of chemicals requires great circumspection, the object of bleaching being merely to destroy foreign substances, which impart a dark colour, or other undesirable properties to the oil or fat. The chief attention of the operator must therefore be directed to so treating the raw material that the fatty matter itself is not acted upon. For this purpose, the amount of chemicals must be limited to the smallest possible quantity, the temperature at which they are allowed to act must be as low as possible, and the time of interaction must be as short as possible.

General methods of bleaching chemically, are—(1) Bleaching by means of oxygen; (2) bleaching by means of chlorine.

(1) Bleaching by means of ozone or oxygen gas is still too uncertain a process to be widely used on a large scale, and is only practised in some special instances. I have examined several ozone processes, but although at the first moment they seemed to effect the bleaching satisfactorily, yet after a time the oils darkened, or as the technical term runs, the colour "reverted."

Bleaching by means of oxygen in *statu nascendi* is chiefly effected by employing manganese dioxide or potassium bichromate and sulphuric acid.

(2) In the processes of bleaching by means of chlorine, bleaching powder, or potassium bichromate and hydrochloric acid are used.

No general rule can be laid down as to which process should be employed in each given case, although it may be stated that tallow is best bleached by means of manganese dioxide, and palm oil by means of bichromate and hydrochloric acid.

The object of bleaching is not only to remove colouring matters for the time being, but to remove them so efficiently that the colour, or even a dark shade, will not "revert" some time after the fat or oil has been bleached. Patents claiming to effect this object appear annually in great numbers, and disappear again when experience has shown that the colouring matter does "revert" to a larger or smaller extent after the material has, *e.g.*, been converted into soap. Thus one of the simplest and most frequently practised processes, that of bleaching tallow, does not produce soaps as good in colour as those made from the freshly rendered tallow. Not only must each kind of fat or oil be considered a special problem, but frequently different varieties of one and the same oil are apt to cause the same difficulties as would a new oil or fat. To mention an example, the bleaching of the softer kinds of palm oil, such as "Lagos" or "Old Calabar," offers very little difficulty. But the harder kinds of palm oil, such as Congo oil, have hitherto withstood all attempts to bleach them.

The above methods of bleaching are, however, inadmissible in the case of those oils and fats which are intended for *edible purposes*. In these cases we must rely chiefly on physical methods. The oils intended for edible purposes must not even be expressed while hot, and the employment of chemicals involving the use of acids must be altogether excluded, as they impart an objectionable flavour which would render the product useless for edible purposes. Treatment with alkalis in one form or another can only be resorted to in a very moderate degree as, for instance, in the refining of cotton seed oil for the table.

The absence of free fatty acids in edible oils and fats is a very important desideratum. Hence, in all refining processes, the complete removal of free fatty acids and of the objectionable products which seem to follow in the wake of the once formed free fatty acids, namely, those which impart to the oil the properties we comprise under the term "rancidity," is the chief aim of the manufacturing processes. Alkalis and alkaline earths are almost exclusively used for these purposes.

The physical method consists chiefly in filtering, with a view to brightening the oils by the removal of the adhering moisture and suspended matter of an albuminoid character, and, if colouring matter is to be eliminated at the same time, in treating with either charcoal or fuller's earth. The latter process is, of course, followed by filtration, in order to get rid of the charcoal or fuller's earth, which absorb and retain the colouring matters.

A further requisite of edible oils is that they should not congeal at temperatures near the freezing point. Most olive oils practically fulfil this demand. In the case of cotton seed oil, however, which is at present used in enormous quantities as an edible oil, or for adulterating high-class edible oils, a solid portion, termed "stearine," separates out at

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a temperature of about 50° F., as exemplified by the specimens before you.

In order to render cotton seed oil suitable for the table, this "stearine" is removed; as the technical term runs, the oil is "demargarinated."

Originally the process of "demargarination" was a natural process, and consisted in allowing the oil to stand in large vessels during the winter, when the "stearine" settled out as a solid mass at the bottom of the vessel, so that the supernatant clear oil could be drawn off. Hence, such "stearine-freed" or "demargarinated" oils are designated "winter oils."

This simple process has, however, become too expensive, owing to the large amount of capital locked up in the enormous quantities of cotton seed oil that had to be stored. Hence, more rapid processes have been introduced. These consist in artificially refrigerating the oil, and filtering off the "stearine" through filter-presses, or removing it by pressure in hydraulic presses. It need hardly be added that in the latter case the whole process must be carried out in artificially cooled rooms.

Through the introduction of demargarinating processes, oils which were objectionable as table oils on account of their separating "stearine," are being added to the range of edible oils. Such oils are arachis oil, and notably that class of Tunisian olive oils which hitherto could not be mixed with the finest Italian and French olive oils, owing to their being exceptionally rich in "stearine."

The industry of *edible fats* has received, during the last decade, a very great impetus; notwithstanding its rapid development, this industry is, however, in my opinion, still in its infancy. One of the most important edible fats, *butter*, claims to belong to the dairy industry. In the interest of the butter industry itself, manufacturing in large establishments should certainly be preferred to the nursing of a kind of home industry under conditions which are not always above suspicion as regards cleanliness. It is just this element which, in addition to the cheapening of food stuffs, has given the enormous impetus to the manufacture of *margarine*.

The prejudice against this product, which popular ignorance connected with a conglomerate of all kinds of oils and fats, even of fish and train oils and refuse fats, or as a Member of Parliament picturesquely termed it about fifteen years ago, "all the greasy rubbish of the world which is being dumped down in this country," is fast disappearing. If we look at the shop windows of our grocers it may be said to have already disappeared. The enormous strides which this industry has made are the best possible proof that it has come to stay.

The first and foremost conditions of this industry are the utmost cleanliness and the employment of the purest and freshest materials, combined with the importance of imparting to the product an attractive and even appetising appearance.

From a sanitary point of view, not the slightest objection can be raised against the substitution of cheaper animal or vegetable fats for the expensive cow-butter, and it is rather desirable that this industry should extend, yielding, as it does, cheap palatable food stuffs and thereby tending to exclude from consumption unhealthy fat from diseased animals, prepared under conditions which do not satisfy the most rigorous demands as regards cleanliness.

The origin of the margarine industry dates back to the times of the Franco-German war, when the needs of the beleaguered population of Paris demanded the resumption of earlier experiments of Mège-Mouriès, which had attracted, a few years before, the attention of the emperor Napoleon.

The fact that butter substitutes lend themselves to fraudulent purposes, as we can unfortunately see every day if we pay some attention to this subject, should be no barrier to the extension of the industry; it is rather the duty of the legislator to render such fraud impossible than to prevent the proper expansion of the margarine industry. Long before margarine made its appearance butter had been adulterated on an immense scale, and the introduction of margarine had a wholesome effect in staying the hands of the adulterator as the formerly favourite adulterants, such as clay, chalk, gypsum, flour, potato pulp, ground white cheese, and similar substances which used to form the stock-in-trade of the adulterator, have disappeared from the list in order to make room for the harmless, but much less readily detectable, margarine.

Margarine consists chiefly of a mixture of animal and vegetable fats. The animal fats are prepared from the freshest beef fat or hog fat. That obtained from beef fat is known as "oleomargarine;" that from hog —neutral lard— is chiefly employed in the United States. The vegetable oils are cotton

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seed oil, arachis oil, and sesamé oil. The vegetable oil must be devoid of free fatty acids and should not possess any unpleasant flavour. Thus, neither maize oil, nor even cotton seed oil, can be used for the finest and best brands of margarine, as the particular flavour of these oils would be noticeable in the finished product.

For the production of oleomargarine, the rough fat is removed from the slaughtered animal as quickly as possible and brought into the works, where it is sorted and the kidney fat is selected. This is carefully washed with warm water and thoroughly cleaned. The cleaned fat is then brought immediately into large, well-aired, artificially cooled rooms to dry and harden, being allowed to hang there suspended from tin hooks for several hours. Another process to secure rapid hardening is to immerse the fat first into iced water.

The hard fat is next cut up and shredded in a shredding machine [various types were shown on the screen] and then ground between rollers. The disintegrated mass is immediately introduced into tin-lined, jacketed vessels, at a temperature not exceeding 45° C., this temperature being maintained by hot water contained in the jacket.

In large establishments different kinds of vessels are used, several types of which I exhibit here on the screen.

At the temperature of 45°C., only a portion of the fat contained in the animal tissues separates on the top of the comminuted rough fat. The settling and clearing is assisted by scattering salt over the surface of the melted fat. This melted portion, appropriately termed "premier jus," is carefully syphoned off and run into clean barrels to be sent to the margarine works proper for further treatment. The "premier jus" is not the whole of the fat contained in the charge, but only the first portion that will exude at a temperature of 45°; the remainder of the fat is recovered from the scraps for other purposes which do not interest us here.

If the margarine be produced in the same works, the "premier jus" is allowed to run into shallow, tin-lined trays, arranged in tiers in a cooled room, when the bulk of the "stearine" separates out in a crystalline condition. For the best qualities of margarine, the "premier jus" is remelted, and allowed once more to settle out, after salt has been added, whereby the last traces of membrane and tissue are precipitated. The cleared fat is allowed to run into large vats, in which it stands from three to five days, at a temperature suitable for the crystallisation of the "stearine."

The crystallised mass from the tins is immediately cut up into small pieces weighing about 3 lbs. each. These are wrapped in canvas cloths, and are then put into hydraulic presses. In large works, where the "premier jus" has been allowed to crystallise in huge vats, the whole crystallised mass is stirred up into a homogeneous pulp which is wheeled to the presses and packed into them in small pieces, wrapped in canvas cloth, holding about 3 lbs. each.

[The "premier jus" presses in actual use in the smallest as well as in the largest establishments were here shown on the screen.]

The oleomargarine—"oleo-oil," as it is termed in the United States—runs out into tanks below the presses, to be worked up for margarine. The solid portion which remains in the presses is sold as tallow stearine.

This oleomargarine is the chief raw material for the manufacture of butter substitutes. It is mixed in special churning machines of the various types I illustrate by lantern slides, with vegetable oils and fats and milk.

The milk department forms, therefore, a substantial portion of the margarine works. On its arrival from the farms the milk must be "pasteurised." As a rule the cream has been taken off before the milk reaches the works, otherwise it is removed by means of a centrifugal machine.

The milk is run, together with the melted oleomargarine and the vegetable oils admixed in accurately weighed off proportions, into churns, in which the whole mass is thoroughly blended. The churning machines consist of oval jacketed vessels, provided with one or two sets of stirring and mixing gear. During the process of churning a constant temperature is maintained by means of steam sent through the jacket of the churn. The object of churning, besides thoroughly mixing the ingredients, is to destroy the tendency of the oleomargarine to crystallise, and to produce a complete emulsion by pulverising the mixture into single globules, such as butter fat forms in milk. When the mass is thoroughly churned, the steam is turned off, and the warm material is cooled by cold water sent through the jacket.

From the churn the cooled margarine is run through wooden shoots into cooling tanks. Whilst running out of the churn the margarine is met in the shoots by a current of

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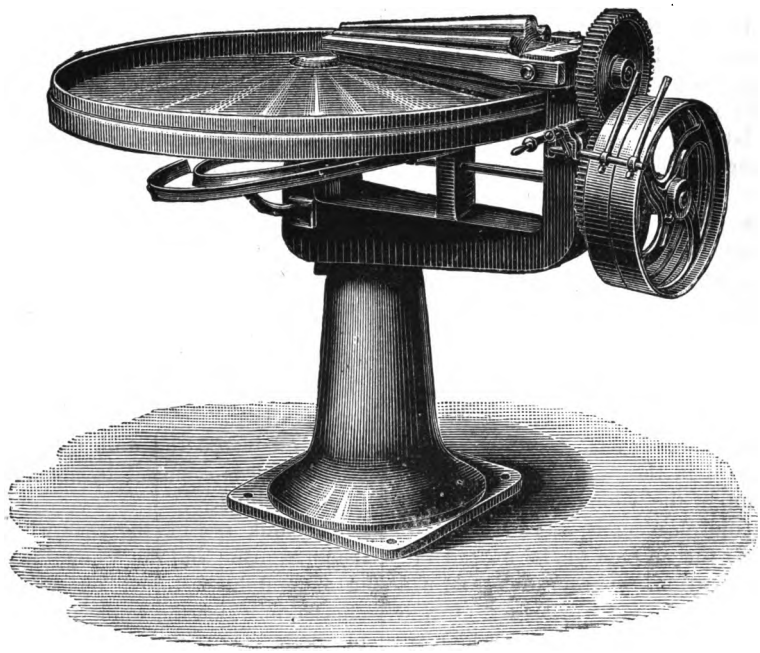
ice-cold water, delivered under high pressure, so that the mass is completely pulverised. The disintegrated globules, after solidifying, somewhat resemble butter granules.

In small works the cooling tanks are built of marble; in larger works they simply consist of large wooden tanks. In other works they form very large storage vessels, built up of tiles.

The solidified margarine is taken out by spades, or by long-handled wooden spoons, and placed in wooden wagons, where the admixed water is allowed to drain off. These wagons [These departments of a margarine works were illustrated by lantern slides.] Like butter, margarine contains water; the proportion of this should however not exceed 10 to 12 per cent. in well-made preparations. From the description given and the lantern slides shown, it will have become apparent that, throughout the whole process, the fatty material is not touched by the hands of the operator. Thus the process compares favourably with that employed in small out-of-the-way dairies, into the minute details of which we had better not inquire.

FIG. 8.



are conveyed to large kneading-machines. They consist of huge, circular wooden tables (Fig. 8), which rotate slowly, whilst at the same time a set of conical, fluted, or specially-shaped rollers move along the top of the revolving tables. The margarine is slowly but thoroughly worked through, so that the particles become homogeneous throughout the whole mass. At this stage colouring matters are admixed.

The margarine is then salted to taste, and submitted to a further thorough kneading and mixing on a machine similar to the one shown in Fig. 8, or in a specially-constructed churning machine (illustrated by a lantern slide).

The margarine is finally moulded into lumps, pats, rolls, or any other desired shape.

The object of the margarine manufacturer is, naturally, to make his product resemble butter as nearly as possible. In order to take away the "tallowy" or exclusively "fatty" taste of the material, some manufacturers, provided the law permit, add butter itself. Others add small quantities of butyric acid, or specially prepared compounds.

An important point is to produce margarine which will froth and "brown" when heated, so that even in cooking the nearest approach to butter is reached. As the property of butter of "browning" and frothing is due to casein and milk sugar, it is evident that the more milk is used in the manufacture of margarine, the nearer will the product approximate to butter. This expedient is largely used in this

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country, but on the Continent, where the law forbids the addition of more than a strictly limited quantity of milk, or its corresponding quantity of butter-fat, a number of curious patents have been taken out for substances purporting to impart the desired property to margarine. Caseïn and other albuminoids are prominent amongst them. The usual crop of excrescences is not wanting in this industry, and even the use of beeswax and vegetable waxes has been patented, although the employment of such substances must be deprecated, as they seriously reduce the digestibility of margarine.

[Tables giving the estimated production of margarine during 1900, and the quantities and kinds of materials used in the production of margarine in the United States will be found on page 925 of my "Technology and Chemical Analysis of Oils, Fats, and Waxes." Macmillan and Co., 1904.]

Another class of edible fats is represented by *lard substitutes*. Their manufacture is in many respects similar to that of butter substitutes, although it is much simpler, since lard substitutes contain no water, and merely represent a mixture of fats. The basis of the lard substitutes should be, of course, lard, with which other oils and fats, such as cotton seed oil and beef fat are intermixed in the melted state.

The enormous quantities of lard substitutes that are produced necessitate rapid cooling of the mass. The simple process of allowing to cool spontaneously in large vessels is too expensive; hence, special cooling machinery, similar to Petit's cooling wheel (see Lecture IV., Fig. 20) is employed. The wheel of Fig. 20 is replaced by a large hollow cylinder through which cooled brine runs, whilst the sheet of cooled lard thus formed is taken off immediately by means of a pump and filled into tierces.

In the early days of this industry the manufacturers of lard substitutes sailed more closely to the wind than the margarine manufacturer. The lard-substitutes sold under such names as "refined lard," "compound lard," were frequently found to contain no lard whatever, being nothing else than judiciously prepared mixtures of beef stearine—the by-product of the margarine manufacture—and cotton seed oil and other vegetable oils. Here also legislation has had to step in to protect the public.

The detection of cotton seed oil in lard became, therefore, one of the most important problems of the public analyst. A rapid means of detecting it is Halphen's test, which reveals the presence of cotton seed oil by a red colouration. However, too much reliance should not be placed on a rapid test like this, since the adulterator has always been able to keep pace with the latest discoveries of science, and has succeeded in nullifying the indications of this test by treating cotton seed oil in such a manner that it no longer shows the characteristic red colouration. Moreover, some help has accrued to the adulterator through the fact that lard from hogs fed on cotton seed cake exhibits a colour reaction similar to that which lard shows which has actually been adulterated with cotton seed oil.

A third kind of edible fats manufactured on a large scale are *vegetable butters* and the hard fats derived therefrom, which I comprise under the name "*chocolate fats*." Vegetable butters were first made from cocoa nut oil and palm nut oil, and prepared for the Indian market, where the native population are forbidden by their religious tenets to consume animal fats. Latterly this vegetable butter has, under a variety of fancy names, such as "lactine," "vegetaline," "cocoaline," "laureol," "nucoline," "albene," "palmine," "cocose," &c., found extensive use at home in confectionery and in the manufacture of margarine, and—it must be feared—is also finding a growing outlet for adulterating cow's butter. From these vegetable butters "chocolate fats" are obtained. The natural chocolate fat is, of course, "cacao butter," which is expressed from the cocoa beans in the course of preparing cocoa. As more cacao butter is obtained from the bean than a properly constituted chocolate should contain, a surplus of cacao butter accumulates in a cocoa works. This surplus is worked up into cheaper kinds of chocolate. Thus a demand has been created for cacao butter. As the natural supply does not suffice, and moreover as cacao butter is the most expensive fat, being even dearer than ordinary cow's butter, there soon arose a demand for a cheap substitute of genuine cacao butter.

Animal fats, such as tallow, are unsuitable for chocolate manufacture, as if not very carefully refined they are apt to impart an unpleasant flavour ("animal flavour") to the finished chocolate.

The best chocolate fat substitutes must, therefore, be prepared from vegetable fats. At present the most suitable substitutes are manufactured from cocoanut and palm nut oils, by removing the softer portions of cocoa

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nut and palm nut oils in a similar manner as is done in the case of working up the "premier jus." The cocoanut and palm nut oils are allowed to crystallise at a slightly elevated temperature, and the crystallised mass is expressed in hydraulic presses. Whereas in the manufacture of oleomargarine the liquid portion is required, in the present case the hard mass left in the press, termed "cocoanut stearine," or "palm nut stearine," is the desired product.

I show here a number of slabs of "stearines" manufactured in the manner described. These samples represent the pure cocoanut oil and palm nut oil products, and are therefore white; for market purposes these products are generally coloured yellow, in order to more closely imitate, or even surpass, in appearance genuine cacao butter. Such products are sold under a variety of fancy names, such as "cacaoline," "cocoline," &c.

These chocolate fats have the drawback that their melting point is somewhat low. Of course, the more of the softer portion is expressed from the cocoanut oil and palm nut oil, the higher will be the melting point. But since the brands having a high melting point are somewhat costly, products of lower melting point find ready entrance into chocolate works, and it is therefore easy to understand why so many kinds of chocolate become soft in the pocket, or even when held in the hand.

In order to impart greater hardness to the chocolate fats they in their turn are "stiffened," *i.e.*, adulterated with small quantities of animal fats, such as tallow, tallow-stearine, &c. It has even been stated that Japan wax is admixed in order to raise the melting point. Also mineral waxes like paraffin wax, ceresin, have been admixed for "stiffening" purposes, but these should be totally excluded as they are indigestible.

The preparation of suitable chocolate fats from vegetable fats of a higher melting point than cocoanut oil or palm nut oil would, in my opinion, bring us nearer to the solution of the problem. I would suggest for this purpose the working up of some tropical vegetable fats, such as margosa oil, mowrah seed oil, &c.

I have dwelt at some length on the industries of edible oils and fats, as I think that this industry has a great future before it. At present it appears to be in a state of transition. From the large number of patents that are being taken out, it is evident that on all sides strenuous efforts are being made to produce these food stuffs in a palatable, appetising, and at the same time comparatively cheap form.

The extent to which margarine is being consumed in this country may be gathered from the fact that during the year 1902 we imported an amount of margarine valued at £2,569,503. It may be safely assumed that at least an equal quantity is being manufactured at home.

Similarly, the extent to which palm kernel oil and cocoanut oil have been used for edible purposes may be best illustrated by the fact that in the year 1902 about 10,000 tons of these fats were worked up in Europe alone for edible purposes.

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LECTURE III.—DELIVERED FEBRUARY 8, 1904.

BURNING OILS.

Whilst in the industry of edible oils it is of paramount importance to remove the free fatty acids, less rigorous demands are made in those cases where oils are used for industrial purposes. But even here, as in the case of burning oils, the amount of free fatty acids must not be too large.

At the present day, when we see electric light everywhere, and gas is supplied for illuminating purposes even in small villages, the mention of burning oils may perhaps strike one as an anachronism. But up to the middle of the last century, olive oil, rape oils, and other vegetable oils were widely, if not exclusively, used as the burning oil of the middle and lower classes, to whom the price of candles was prohibitive.

It is only with the advent of paraffin oil that the use of fatty burning oils has become restricted. But even at the present day large quantities are still required for burning purposes, as the collection of burning oils exhibited on the table demonstrates. To take an example, in Norway whale oil is largely used nowadays for illuminating purposes. Whale oil and seal oil, especially of the water white qualities, are still in demand for lighthouses.

Railway companies still use enormous quantities of rape oil in this country, just as in America lard oil, and in Italy olive oil, are required for burning on railways (illuminating signals, &c.).

In the case of burning oils, refining must be carried out somewhat carefully, and the amount of free fatty acids must not exceed 3 to 5 per cent., as otherwise the wick of the lamp easily becomes clogged. Of what great importance this is in railway signalling can well be imagined, when the fact is borne in mind that many lamps are relied upon to burn brightly for a certain number of hours without requiring attention.

LUBRICATING OILS.

Another class of oils which must also be somewhat carefully refined is that of lubricating oils. The chief fats and oils used for lubricating are tallow, lard oil, tallow oil, olive oil, rape oil, and I may add sperm oil, although chemically considered it is not a fatty oil, but falls under the definition of a wax. Before mineral oils appeared in the market, these oils were used exclusively as lubricants, but since the enormous industry of mineral lubricating oils has been created, the importance of the fatty oils in this respect has greatly diminished, although they still play a very considerable part in the manufacture of lubricating oils. It cannot be contested that a certain admixture of fatty oils with mineral oils gives better results in the lubricating of steam cylinders than mineral oils alone.

Railway companies employ rape oil as the lubricating oil *par excellence*.

In this connection, it may strike one as an anomaly that India exports practically her total yield of rape seed to this country, and takes back rape oil, which is almost exclusively used for lubricating the axles of her railway locomotives.

Olive oil is in this country too expensive for lubricating purposes, for the cheaper kinds contain too large quantities of free fatty acids, a fact which, of course, precludes their use.

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Tallow oil and lard are still employed to a large extent.

Drying oils are utterly unsuitable for lubricating purposes, as they resinify rapidly and clog up the machinery. Also semi-drying oils, like cotton seed oil and maize oil, are unsuitable. Since cotton seed oil is extensively employed in other directions, the advertising of this oil in this respect has ceased, and the goodwill thereof has fallen to maize oil, the enormous quantities of which are still seeking new outlets.

All the oils mentioned are readily miscible with mineral oils, and hence the "blends" prepared from mineral oils and fatty oils are of the greatest possible variety. The only fatty oil which will not mix in all proportions with mineral oils is castor oil; and as castor oil, on account of its high specific gravity, is a desirable ingredient in lubricating oils, the expedient is resorted to of mixing castor oil first with a fatty oil, say tallow oil, and then adding mineral oil.

The high price at which castor oil stood some years ago, led to the manufacture of oils simulating castor oil in respect of high specific gravity and viscosity. These oils are known under the name of "blown" oils or soluble castor oils. They are made by blowing a current of air into the slightly-warmed oils in a machine such as I show on the screen, when oxygen is absorbed and so much heat generated, that the reaction proceeds without any further heat being applied. Sometimes the rise of temperature is so great that the oil must be cooled. Especially suitable for the manufacture of these blown oils are the semi-drying oils, The samples of blown rape oil, blown cotton seed oil, blown ravison oil, blown maize oil, and blown seal oil I show here, illustrate the wide range of these oils.

Opinions as to the suitability of these oils for lubricating purposes are still conflicting, objection being taken to them by many engineers on account of their liability to gum and their low flash points.

Paint Oils.

A great industry, consuming large quantities of oils, is that of paint oils. The paint oil *par excellence* is linseed oil. A few years ago, when the price of linseed oil was twice as high as it is at present, substitutes were largely in demand. The best substitutes will, of course, be those oils which are most nearly related to linseed oil, and the proper linseed oil substitutes must therefore be looked for amongst vegetable drying oils. As possible linseed oil substitutes, I show here candle nut oil, safflower oil, tung oil, niger seed oil, poppy seed oil, walnut oil. Although at present, on account of the fall in price of linseed oil, the stimulus for the production of these oils has been removed, they may, at any time when the turn of the wheel brings forth again high prices for linseed oil, force themselves on the attention of the manufacturer. The safflower oil of India, and the candle nut oil of the South Sea Islands may then deserve more attention than is at present bestowed upon them.

Especial varieties of paint oils are those which are required for artists' use, and here with the exception of poppy seed oil and walnut oil, which find great favour with artists for the best white paints, linseed oil bleached by sunlight is employed.

Recently several processes for bleaching linseed oil by ozone have been worked on an experimental scale, but so far, and I speak from experience, having investigated myself several ozone processes, the natural oil is not surpassed by ozonised oils.

Semi-drying oils are unsuitable, and although maize oil, enormous quantities of which were pressed heavily on the American market a few years ago, has been widely advertised as a paint oil, it must stand condemned as unsuitable for that purpose.

Boiled Oils.

The value of the drying oils rests on a remarkable property they possess, viz., that of absorbing oxygen from the air. Linseed oil is capable of taking up as much as 20 per cent. of its own weight in the course of about three days, passing from its oily state through an intermediate stage of a viscous, then tacky substance, until it is converted into a thin, elastic, flexible skin. The rapidity of drying can be much accelerated by the process of "boiling" the oil, that is, heating the oil with certain metallic oxides to a high temperature.

The invention of this process of "boiling" has been ascribed to the Dutch painter, Van Eyck; and we can well imagine how empiricism led an artist who had to mix the pigments with oil to discover such a process. Although several centuries have elapsed since this discovery was made, we are still unable fully to understand the chemical change which takes place when an oil boiled with metallic oxide dries.

For some time it was assumed that the oil

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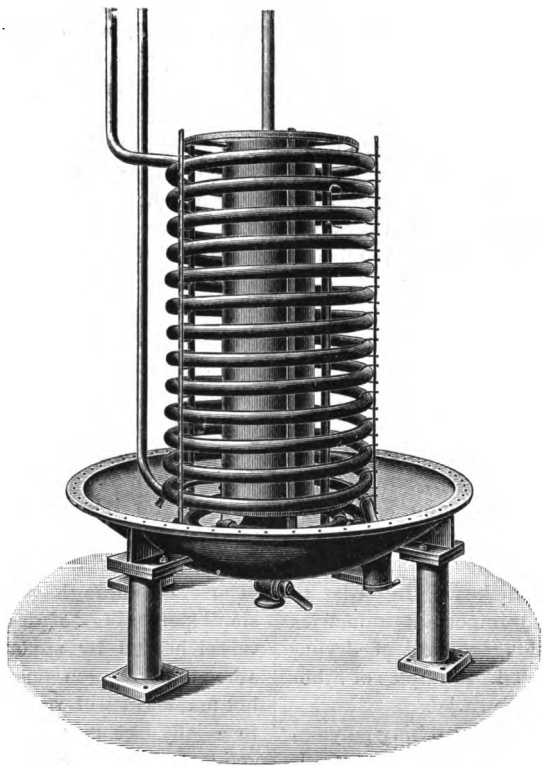
itself became oxidised, the glyceridic part of the oil being attacked in the first instance. But this view must be rejected as erroneous, since "boiled" oil retains almost its whole quantity of glycerin. Moreover, practice has shown that the glyceridic part of boiled oil is a necessary ingredient, and several attempts, for which patents have been taken out, to prepare boiled oils from the fatty acids, after the removal of the glycerin, have led to useless products. The explanation was then suggested that the metallic oxides act as oxygen carriers during the boiling, but the process of boiling certainly does not consist in an oxidation of the oil, since if oxidation really does take place, it cannot exceed a very slight amount. In the investigation of an ozone process, I have noticed that oils treated with oxygen acquire all the properties of boiled oils, although chemically speaking they had undergone a very slight change only.

Furthermore, recent progress has shown that a high temperature is not required for the preparation of boiled oils, as we are able to obtain oils having the property of boiled oils by carefully grinding linseed oil in the cold with manganese borate.

Much lower temperatures than are required in the old process of boiling have been found sufficient. Thus at present the bulk of the boiled oils is obtained by heating linseed oil with driers to a temperature of 150°C only. The process is carried out by introducing the oil into a cylindrical vessel, provided with a heating coil and an agitating gear, so as to produce an intimate intermixture between oil and drier whilst they are heated to the desired temperature. The internal arrangement of a modern oil boiling vessel is illustrated by Fig. 9. Here the cylindrical part of the vessel, to which a small steam engine driving the agitating gear is attached, has been removed in order to show the heating coil and stirring apparatus.

FIG. 9.



The temperature employed in boiling can be still further lowered since modern driers have been introduced, especially those known as *liquid driers*. These liquid driers consist of a solution of lead linoleate or even of resinate in boiled oil or linseed oil.

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A very complete collection of driers which are obtainable in the trade is before you on the table. I have added a drier which I prepared on a somewhat large scale from tung oil and have termed "tungate drier."

These driers, especially the liquid driers, have led to a great deal of secretmongering. They are sold under a variety of fancy names of which the best known is perhaps "terebene." A few per cent. of these driers added to linseed oil at temperatures of 120-150° C. is able to impart to the oil the properties of boiled oil. The mania for cheapening has even gone so far that "boiled" oils are prepared by merely pouring a solution of these driers into linseed oil in the cold. Such oils, which the Americans in their characteristic jargon call "boiled through the bunghole" are distinctly inferior to oils prepared by the aforementioned processes.

Now, if a mere dissolving of the drier in the oil is sufficient, then no important chemical change can have taken place. Yet the only explanation which commends itself at present, and in support of which I have published elsewhere a number of experiments, is that the oil becomes polymerised. The first outward sign of this consists in the oil acquiring a higher specific gravity. This explanation gains support in the fact that by merely heating linseed oil without any driers an increase of specific gravity, or polymerisation, takes place.

Processes based on this reaction have been practiced very extensively for many years, and I need only mention the words "printing ink" and "lithographic varnishes" in order to recall to your mind the important industries which are based on this property of drying oils to become polymerised. (Samples of lithographic varnishes were shown.)

Another illustration of a far-reaching polymerisation is given by the example of *tung oil*. If this oil is heated to 180° C. for several hours, or to 250° C. for a short time, it solidifies to the jelly-like mass I show here.

The boiled oils find extensive employment not only in our ordinary paints; enormous quantities are used in the *varnish industry*. The theory of this manufacture is simple. It consists in dissolving suitably-prepared gums and resins (a representative selection of which is exhibited on the table) in linseed oil and "boiling" the mixture. The "varnish oil" so obtained is thinned down with oil of turps. Simple as the manufacture appears, this industry is still surrounded by an enormous amount of secretmongering, and the light of scientific investigation has so far hardly penetrated into this industry. Each varnish maker jealously guards his recipes, and envelops his mode of manufacture in an atmosphere of the deepest mystery.

It must be hoped that industry will emerge from its darkness through scientific progress, much as the soap industry has emancipated itself, to its great advantage, from the secrecy which the foreman soap boiler found it to his interest to maintain.

Oxidised Oils.

If the oxidation of linseed oil is carried further until the maximum amount of oxygen is absorbed, we obtain the "solid linseed oil" (samples of which, made by various processes, I show here), representing an elastic jelly-like mass. It is prepared by allowing linseed oil, previously boiled with a drier so as to accelerate the oxygen absorption, to run over a light cotton fabric—"scrim"—hanging from the ceiling of a high building kept at a temperature of about 100° F., so that the oil, whilst trickling down from the top of the house, is capable of absorbing rapidly the maximum amount of oxygen. A portion of the oil solidifies on the fabric, the oil which drains off at the bottom being pumped up again, and allowed to run down, until the layers of the solid mass have reached, after several weeks, a thickness of about half an inch. This process is termed the "scrim process;" the solidified oil obtained by this method is termed "scrim oil."

Another method consists in passing a current of oxygen through linseed oil mixed with a small percentage of drier in a closed jacketed vessel heated by steam, until the maximum amount of oxygen has been absorbed. The hot mass will still run, but after cooling it sets to a jelly-like mass which is dry enough and solid enough to be packed into bags. These materials form one of the chief ingredients of "linoleum," the invention of Walton and his successors. For this purpose, the "scrim oil" is mixed with rosin and ground cork, rolled on a jute canvas backing, and is finally seasoned at a temperature of 75° before it is placed on the market in its well known form.

Vulcanised Oils.

If in the last described process we substitute sulphur for oxygen, we obtain that class of oils which are best described as "vulcanised oils." The treatment is similar to that which indi

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rubber undergoes in the vulcanising process, and just as in india-rubber vulcanising we have two processes, viz., the "hot cure" (treating the india-rubber with sulphur at a high temperature), and the "cold cure" (treating with sulphur chloride at a low temperature), so we can produce the vulcanised oils either by treatment with sulphur at a higher temperature, or with sulphur chloride at the ordinary temperature.

The reaction is almost instantaneous in the case of castor oil; hence I am able to show it here on a small scale. Although I am tempering the reaction by first dissolving both the oil and the sulphur chloride in carbon bisulphide, you note that by stirring together these two solutions a solid product is formed in about half a minute, so that on turning the capsule upside down a solid product falls on the table.

Other oils, such as linseed oil and rape oil, require a little longer time, and a somewhat elevated temperature. The products so obtained have acquired commercial importance. They form a mass possessed of not very great elasticity; and are chiefly employed to adulterate ("cheapen," as it is called euphemistically) india-rubber goods. The great deterioration which india-rubber goods exhibit (during the last decade or two) is due to the extensive employment of these substitutes.

Sulphonated Oils.

Oils and fats undergo a somewhat deeper change when they are treated with concentrated sulphuric acid. They combine with this acid and form water-soluble products. On this reaction is based the industry of *turkey-red oils*.

This class of oils is prepared by allowing concentrated sulphuric acid to run into castor oil slowly, with constant stirring, taking care that a temperature of 35°C. is not exceeded. The product is then mixed with water and allowed to settle out; the lower layer is drawn up and washed with a solution of sodium sulphate until the acid is practically removed. Finally ammonia is added until the sample gives a clear solution with a small quantity of water. [Experiment shown.]

At times, when castor oil was high in price, cheaper substitutes, such as cotton-seed oil, &c., were used. At present, however, the price of castor oil is so low that it would not pay to employ anything but the genuine oil.

The manufacture of turkey-red oils forms as it were an intermediate link between those industries in which the glycerides undergo a more or less pronounced chemical change but are not saponified, and those industries which are based on the hydrolysis (saponification) of oils and fats. The latter industries comprise the manufacture of *stearine candles*, *soaps*, and *glycerin*.

Hydrolysis of Oils and Fats.

In order fully to understand the chemical reactions which take place, and lie at the basis of these industries, it is necessary to consider the theoretical constitution of the glycerides of which the natural oils and fats consist.

The glycerides may be looked upon as salts formed by the union of the tribasic substance glycerol (glycerin) $C_3H_5\begin{matrix}OH\\OH\\OH\end{matrix}$ and three molecules of fatty acids. The latter may be represented by the formula R.OH in which R denotes the radicle (radical) of any fatty acids. The formation of the glycerides may therefore be expressed by the following equation—

$$C_3H_5\begin{matrix}O.H\\O.H\\O.H\end{matrix} + 3\,R.OH = C_3H_5\begin{matrix}O.R\\O.R\\O.R\end{matrix} + 3\,H.OH \quad (1)$$

Now, if instead of 3 ROH, *i.e.*, 3 molecules, only *one* molecule of fatty acid were allowed in the equation (1), the substitution of only one hydrogen atom "H" in the glycerol, by one radicle of the fatty acid "R," can take place. We should then obtain a substance having the formula—

$$C_3H_5\begin{matrix}O.R\\O.H\\O.H\end{matrix}$$

A compound having this composition is termed a *monoglyceride*.

According to the position which the "R" takes up in the molecule, two different monoglycerides are possible, as expressed by the two formulæ:—

$$C_3H_5\begin{matrix}O.R\\O.H\\O.H\end{matrix} \qquad C_3H_5\begin{matrix}O.H\\O.R\\O.H\end{matrix}$$

If we denominate a monoglyceride represented by the first formula α-monoglyceride, a monoglyceride represented by the second formula would be appropriately termed β-monoglyceride.

Hitherto, glycerides of the α-form only have been obtained, but there should be no difficulty in preparing also the β-compounds.

If we substitute in the above equation (1) *two*

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hydrogen atoms by two radicles of fatty acids, we obtain a compound of the general formula—

$$\begin{matrix} & O.R \\ C_3H_5 & O.R \\ & O.H \end{matrix}$$

Substances having this composition are termed *diglycerides*.

It is evident from the last formula that here again two different ("isomeric") diglycerides are possible, according to the position of the radicles "R" in the molecule. This is expressed by the two following formulæ:—

$$\begin{matrix} & O.R \\ C_3H_5 & O.H \\ & O.R \end{matrix} \qquad \begin{matrix} & O.R \\ C_3H_5 & O.R \\ & O.H \end{matrix}$$

The first compound is termed α-diglyceride, and the second β-diglyceride.

Representatives of both the α- and the β-compounds have been prepared in the laboratory.

[Lantern slides were then exhibited, giving in tabular arrangement a list of the monoglycerides and diglycerides prepared hitherto.*]

If in the above equation (1) all three hydrogen atoms are replaced by "R," we obtain the *triglycerides*. I show in a lantern slide those triglycerides which have been obtained up to the present in a state of purity.†

Hitherto it has been assumed that the naturally occurring glycerides represent mixtures of triglycerides in which all three radicles of the fatty acid are of *one and the same* composition. Hence most natural oils and fats were looked upon as consisting of mixtures of the most frequently occurring triglycerides:—Tripalmitin, tristearin, and triolein.

The general formula of the triglycerides is therefore expressed by the following formula—

$$\begin{matrix} & O.R \\ C_3H_5 & O.R \\ & O.R \end{matrix}$$

Theoretically, we may assume that the fatty acid radicles "R" may be of different composition. Hence, if we denominate the glycerides of the formula—

$$\begin{matrix} & O.R \\ C_3H_5 & O.R \\ & O.R \end{matrix}$$

simple glycerides, such glycerides in which the acid radicles are not alike, must be termed *mixed glycerides*.

It is evident that only *one* form of a simple triglyceride can exist. But if radicles of different composition enter into combination with glycerol, then we have two possibilities.—

1. Two "R's," denominated R_2 and R_2, are alike, but differ from the third radicle, denominated R_1.

2. All three "R's," denominated R_1, R_2, R_3, differ from each other.

It will be seen that in the first case *two* different triglycerides are possible, as shown by the formulæ:—

$$\begin{matrix} & O.R_1 \\ C_3H_5 & O.R_2 \\ & O.R_2 \end{matrix} \qquad \begin{matrix} & O.R_2 \\ C_3H_5 & O.R_1 \\ & O.R_2 \end{matrix}$$

In the second case *three* isomerides are possible, as explained by the following formulæ:—

$$\begin{matrix} & O.R_1 \\ C_3H_5 & O.R_2 \\ & O.R_3 \end{matrix} \qquad \begin{matrix} & O.R_2 \\ C_3H_5 & O.R_1 \\ & O.R_3 \end{matrix} \qquad \begin{matrix} & O.R_1 \\ C_3H_5 & O.R_3 \\ & O.R_2 \end{matrix}$$

To repeat, whereas only *one* simple triglyceride of any fatty acid can exist, there may exist *two* mixed triglycerides in which two different acid radicles (R_1 and R_2) are combined with one C_3H_5 group, and *three* different mixed triglycerides in which all three acid radicles, R_1, R_2, R_3, are different.

We are therefore confronted with the likelihood of meeting in the natural products representatives of all theoretically possible glycerides. Hitherto, hardly more than a beginning has been made in the investigation of this somewhat complicated-looking problem. Only a few years ago the first mixed glyceride—*oleodistearin*—was discovered in Mkányi fat, and it is characteristic that this discovery has been made in the course of an examination of one of the foreign vegetable fats which the German Government is having examined in an institution which, in this respect, fulfils similar functions to those of our Imperial Institute.

The methods by which the *mixed* glycerides are isolated from the natural oils and fats are still of an exclusively scientific character. Such triglycerides have since been discovered in olive oil, cacao butter, lard, and human fat. It is impossible to say at the present moment what will be the outcome of the large vista of researches thus thrown open. To the practical manufacturer who merely looks to the obtainment of mixed fatty acids and glycerin, it is immaterial whether the natural oils and fats consist of mixed glycerides or of mixtures of simple glycerides.

On reversing the above given equation (1), and writing it in the following manner, taking M to stand for a hydrogen atom, it reads to mean

* Compare Lewkowitsch, "Laboratory Companion to the Oils and Fats Industries," Tables 1 and 2, pp. 8 and 9; as also Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats, and Waxes," 1904, pp. 4 to 7.

† Compare "Laboratory Companion to the Fats and Oils Industries," Table 3, pp. 10 and 11; also "Chemical Technology and Analysis of Oils, Fats, and Waxes," 1904, pp. 7 16.

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that the triglycerides are decomposed by water into fatty acids and glycerol (glycerin)—

$$C_3H_5\begin{matrix}O.R\\O.R\\O.R\end{matrix} + 3\,MOH = C_3H_5\begin{matrix}O.H\\O.H\\O.H\end{matrix} + 3\,R.OM \quad . . \quad (2)$$

[If M denotes a monovalent metal, such as sodium, Na, or potassium, K, then the equation would mean that the triglyceride is decomposed by sodium hydrate (or potassium hydrate) into sodium (or potassium) salts of fatty acids and glycerin.]

Just as we have seen above, that by bringing together glycerol (glycerin) and successively three molecules of fatty acids, we can trace the formation of a triglyceride through the intermediate stages of a monoglyceride and diglyceride, so can we assume that the last equation (2) is merely a summary of three reactions, taking place one after the other. This is expressed by the following three equations :—

$$C_3H_5\begin{matrix}O.R\\O.R\\O.R\end{matrix} + M.OH = C_3H_5\begin{matrix}O.H\\O.R\\O.R\end{matrix} + R.OM \quad . . \quad (2a)$$

$$C_3H_5\begin{matrix}O.M\\O.R\\O.R\end{matrix} + M.OH = C_3H_5\begin{matrix}O.H\\O.M\\O.R\end{matrix} + R.OM \quad . . \quad (2b)$$

$$C_3H_5\begin{matrix}O.M\\O.M\\O.R\end{matrix} + M.OH = C_3H_5\begin{matrix}O.H\\O.M\\O.M\end{matrix} + R.OM \quad . . \quad (2c)$$

These equations express by means of chemical symbols that at first (equation 2a) *one* radicle of fatty acid is replaced by H with the formation of the diglyceride ; that this diglyceride is then further acted upon (equation 2b) by one M.OH with the formation of the monoglyceride, and that the latter is finally converted (equation 2c) by a third molecule of M.OH into glycerol (glycerin), and the third molecule of fatty acids. On adding the three equations together, we arrive of course at the equation (2) given above.

It would appear that for practical purposes it is pretty immaterial whether the reaction takes place in three stages, or in one stage only, as the manufacturer is solely concerned with the final result. Still, from a theoretical point of view, it is interesting to ascertain whether these three stages can be shown actually to occur. Once the theoretical possibility is established, practical conclusions will follow in the natural course.

Now, I have been able to show by actual experiments that hydrolysis does take place in three stages. It cannot be expected that these three stages follow each other consecutively, in distinct succession, or, in other words, we cannot expect to find that the whole mass of triglycerides is at first hydrolysed exclusively to diglycerides, as indicated by the equation (2a), that the diglycerides are then broken down to monoglycerides as shown by the equation (2b), and that, finally, the monoglycerides so formed are converted into glycerol and free fatty acids. We shall rather find that all the three phases expressed by the above three equations take place concurrently, so that at one and the same time one molecule of diglyceride may have been broken down to monoglyceride and fatty acid, or one molecule of monoglyceride to glycerol and fatty acid, whilst one molecule of triglyceride is still intact, or passes through the first phase. Therefore, on bringing about hydrolysis very rapidly, we cannot always observe experimentally the intermediate, transitory phases. If, however, hydrolysis (saponification) be effected somewhat slowly, we shall be able to find in the partially saponified mass : (1) unsaponified triglyceride, (2) diglyceride, (3) monoglyceride, (4) glycerol (glycerin), and (5) free fatty acids.

Now if a large quantity of fat is boiled up, say with caustic soda, in an open soap pan, a sample taken out of this pan before the saponification has been completed will contain all these glycerides. In the present state of our chemical knowledge it is very difficult, if not practically impossible, to separate substances so closely allied. I therefore tried to prove the presence of these intermediate glycerides in an indirect manner.

If monoglycerides and diglycerides were present, then it should be possible to convert them again into a triglyceride by combining them with a suitable fatty acid radicle. If, for instance, a diglyceride be heated with acetic anhydride, then a mixed triglyceride will be formed, of which two radicles are the same as before, whilst the hydrogen of the OH group is replaced by the radicle of acetic acid. Similarly, in a monoglyceride the two hydrogen atoms of the OH groups will be replaced by two radicles of acetic acid. Now the radicle of acetic acid can easily be split off again, and determined by quantitative methods. The amount of the acetic acid we thus obtain is a measure—not an absolute measure, but still a measure—of the amount of mono- or di-glycerides that are present in the sample.

The manner in which the experiments have been carried out cannot be explained here.* It must suffice to state that the amount of

* Compare Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats, and Waxes," Macmillan and Co., 1904, p. 268.

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acetic acid is expressed in terms of potassium hydrate with which it combines to form potassium acetate, and that the number so found is termed in fat analysis, the "acetyl value."

If saponification took place exclusively in the manner indicated by equation (2)—*i.e.*, if the glycerides are hydrolysed straightway into fatty acids and glycerol (glycerin) — then samples taken at any intermediate stages of saponification before the completion of hydrolysis should exhibit no acetyl value, but if there be present mono- and di-glycerides, then the samples taken must show a distinct acetyl value.

I have tested these views experimentally by saponifying tallow and cotton seed oil in the laboratory on a somewhat large scale, exactly simulating the operations taking place in a chemical works. Care was taken to conduct the saponification somewhat slowly, so as the more readily to get hold of the intermediate products.

In the following four tables, I present a selection from a large number of experiments I have carried out, saponifying slowly the fatty substance, and examining samples taken out from time to time, whilst the mass underwent hydrolysis (saponification).

TABLE V.—Saponification of Tallow with Caustic Soda (Lewkowitsch).

Partially Saponified Tallow.	Acid Value.	Acetylated Product.		
		Acetyl Value.	Hehner Value.	Saponification Value.
Sample No. 1	12·2	17·1	94·4	207·9
,, ,, 2	12·8	24·3	94·7	210·2
,, ,, 3	20·9	18·9	94·9	206·6
,, ,, 4	31·4	9·7	95·8	203·1
,, ,, 5	45·4	15·3	96·0	208·15
,, ,, 6	77·9	11·2	97·0	206·7
,, ,, 7	105·8	52·03	..	237·65
,, ,, 8	126·8	65·6	..	252·5
,, ,, 9	145·3	78·9	..	269·0
,, ,, 10	152·4	61·8	..	252·7
Fatty Acids, obtained with Alcoholic Potash, Acetylated	..	8·8	99·5	212·8

TABLE VI.—Saponification of Tallow with Lime (Lewkowitsch).

Partially Saponified Tallow.	Acid Value.	Acetylated Product.		
		Acetyl Value.	Hehner Value.	Saponification Value.
Sample No. 1	20·6	13·9	93·3	210·05
,, ,, 2	40·9	22·3	93·5	215·3
,, ,, 3	79·0	16·6	93·5	214·6
,, ,, 4	46·1	15·7	94·5	212·3
,, ,, 5	50·98	27·9	93·87	221·4
,, ,, 6	59·6	28·0	93·6	223·75
,, ,, 7	114·2	..	94·97	216·5
,, ,, 8	122·05	27·2	95·5	226·7
,, ,, 9	110·9	42·0	93·8	239·35
,, ,, 10	128·4	..	95·57	218·7
Fatty Acids, obtained with Alcoholic Potash, Acetylated	..	6·7	99·5	212·8

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TABLE VII.—Saponification of Cotton Seed Oil with Caustic Soda (Lewkowitsch).

Partially Saponified Oil.	Acid Value.	Acetylated Product.		
		Acetyl Value.	Hehner Value.	Saponification Value.
Sample No. 1	1·63	14·15	..	..
„ „ 2	3·4	25·9	..	221·7
„ „ 3	18·4	27·3	..	226·7
„ „ 4	39·7	21·6	..	232·85
„ „ 5	45·3	29·8	..	222·65
„ „ 6	57·0	29·5	..	231·4
„ „ 7	71·8	25·0	..	225·3
„ „ 8	95·5	20·8	..	223·8
„ „ 9	108·2	25·85	..	235·0
„ „ 10	113·7	22·4	..	221·2
„ „ 11	161·0	21·7	..	219·9
Original Oil, Acetylated	..	15·8	..	..
Fatty Acids, obtained with Alcoholic Potash, Acetylated	201·2	17·9	..	..

TABLE VIII.—Saponification of Cotton Seed Oil with Lime (Lewkowitsch).

Partially Saponified Oil.	Acid Value.	Acetylated Product.		
		Acetyl Value.	Hehner Value.	Saponification Value.
Sample No. 1	0·5	14·9	94·5	206·3
„ „ 2	0·6	20·0	92·84	209·2
„ „ 3	16·0	43·15	92·0	230·1
„ „ 4	17·6	59·2	89·1	240·0
„ „ 5	19·9	28·3	92·35	215·3
„ „ 6	53·4	24·9	93·8	214·8
„ „ 7	73·2	32·4	93·6	223·4
Original Oil, Acetylated	0·0	11·7	93·5	..
Fatty Acids, obtained with Alcoholic Potash, Acetylated	199·45	13·8	99·4	216·4

The first column of Table V. gives the order in which the samples were taken.

In the second column the progress of saponification is indicated. A completely saponified sample would have shown the figure of about 200.

Here we are interested only in the column headed "Acetyl value." The original fat showed in a blank test (which must be carried out for the sake of comparison) an acetyl value of 8·8, and if saponification had not taken place in stages, all samples of the partially saponified mass should have given the same value, viz., 8·8. A glance at the tables proves that widely deviating numbers were obtained. At the same time it will be noticed that the numbers do not vary in a regular manner, but in zigzag fashion. This proves that all the reactions indicated by the above-given equations (2a, 2b, 2c) are taking place simultaneously.

Tables VI., VII., VIII. demonstrate the same fact. The experiments detailed in Table No. VI., represent the process carried out in the old candle-making processes (see Lecture IV.).

In Table No. VII., which illustrates the saponification of cotton seed oil with caustic soda, the zigzag-like progress of saponification is not so distinctly pronounced as in the aforementioned cases, no doubt owing to the saponification having occurred somewhat rapidly

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so that all phases seem to have taken place more or less at the same time. On retarding the rapidity of saponification, as shown in Table VIII., when cotton seed oil was saponified with lime and the samples were taken out in somewhat rapid succession (for the last sample had only the acid value 73·2, which means that about 36 per cent. of fat only had been saponified completely), the successive stages become again noticeable. The irregularly moving acetyl values, culminating in the number 59, prove that saponification had taken place in consonance with my views.

The numbers contained in columns 4 and 5 headed "Hehner Value" and "Saponification Value" respectively demonstrate the same law.

[A number of lantern slides were then shown, in which the results were expressed graphically by means of curves.]

Hitherto, I have considered *water* only as the means employed for breaking up the molecule of glycerides, or, to use the scientific term, for "hydrolysing" the glycerides. Since it has been proved experimentally that if water be absent hydrolysis cannot occur, we must accept the view, which I consider the correct one, that water is the hydrolysing agent. It would then follow that those reagents which are employed on a large scale for saponification, such as lime and the caustic alkalis, only act as catalysing agents in that they accelerate the reaction which takes place when oils and fats are hydrolysed by means of water.

As we shall see in the next lecture, it is indeed possible to saponify fats by water alone. Here I wish to lay stress on the fact that water is the hydrolysing agent, and that water alone is capable of effecting hydrolysis if sufficient length of time be allowed. This is proved for instance by the fact that if fats are exposed to the action of moisture (the atmosphere), hydrolysis will gradually set in. Of course, such hydrolysis takes place at a very slow rate only and may require many years for its completion much as the decomposition of felspar requires centuries for its completion. This slow process of hydrolysis is well known. It is expressed in common parlance by the word "rancidity," although this term also includes the further subsequent changes which the fatty acids, set free by the spontaneous hydrolysis,* undergo.

From a practical point of view, it is therefore necessary to assist the reaction by suitable agents, so that it may be completed within a short time. In order to understand better the practical processes that will be detailed in the next lecture, it will be advisable to consider and follow here, step by step, from a theoretical point of view the influence of these factors and reagents which are used on a large scale to accelerate the hydrolysing action of water.

To begin with, high temperature is capable of accelerating hydrolysis. If we heat fats with water to a temperature of 200-300°C., the hydrolysis into fatty acids and glycerol (glycerin) will take place within 8 to 10 hours. The comparative rapidity with which the reaction proceeds must be ascribed to some extent to the thorough intermixture between fat and water, since by pulverising the material a very large surface can be exposed to the action of the water.

Another means of accelerating the hydrolysing action of water is *hydrochloric acid*, which obviously does not take part in the chemical change. This is clearly shown by a number of experiments which I have carried out. They are reproduced in the following three tables:—

* I have suggested for this chemical change the term: "Auto-hydrolysis" (see Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 1904, p. 23).

TABLE IX.—Hydrolysis of Oils and Fats by Means of Hydrochloric Acid, Specific Gravity 1·16 (Lewkowitsch).

100 grms. of Oil or Fat boiled with 100 c.c. of Acid.

Oil or Fat.	Original Acid Value.	Acid Value after 24 hours' boiling.	Acid Value of completely Hydrolysed Oil or Fat.
Cotton seed	0·35	143·9	202
Whale	6·01	157·3	195
Rape	2·16	131·7	185
Lard	1·25	140·3	201
Tallow	11·15	150·0	200
Cocoanut	18·75	204·9	200
Castor	1·22	49·14	190

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TABLE X.

HYDROLYSIS OF OILS AND FATS BY MEANS OF HYDROCHLORIC ACID, SP. GR. 1·16 (Lewkowitsch). 100 grms. of Oil or Fat and 100 c.c. of Acid; fresh acid used after each sample had been taken.

Oil or Fat.	Original Acid Value.	Acid Values after									Acid value of completely hydrolysed Oil or Fat.
		2 hrs.	7 hrs.	9 hrs.	12 hrs.	14 hrs.	16 hrs.	18 hrs.	20 hrs.	22 hrs.	24 hrs.	
Cotton seed	0·35	18·42	79·6	95·51	116·2	136·4	144·9	155·7	164·8	168·2	175·8	202
Whale	6·01	26·69	101·3	120·3	142·7	155·4	162·3	170·0	172·0	...	...	195
Rape	2·16	19·66	75·06	89·57	107·2	120·1	127·3	134·2	140·3	144·0	151·8	185
Lard	1·25	14·51	84·78	116·8	139·8	149·4	152·1	162·7	168·0	173·0	177·0	201
Tallow	11·15	43·39	112·5	131·7	153·2	167·0	173·3	178·9	183·3	185·2	186·8	200
Cocoanut	18·75	79·73	184·2	210·5	221·4	230·8	233·4	239·8	241·1	246·1	250·1	260
Castor	1·22	44·4	47·3	49·0	51·4	51·4	47·9	49·2	46·8	44·4	41·64	190

TABLE XI.

HYDROLYSIS OF OILS AND FATS BY MEANS OF HYDROCHLORIC ACID, SP. GR. 1·16 (Lewkowitsch). 100 grms. of Oil or Fat, containing Free Fatty Acids, and 100 c.c. of Acid; fresh acid used after each sample had been taken.

Oil.	Original Acid Value.	Acid Values after									
		2 hrs.	4 hrs.	7 hrs.	9 hrs.	12 hrs.	14 hrs.	16 hrs.	18 hrs.	20 hrs.	22 hrs.	24 hrs.
Cotton seed	10·51	37·69	71·1	88·73	94·85	103·9	113·6	117·1	119·7	125·6	132·1	140.3
Whale	15·16	41·44	85·84	105·0	123·2	147·3	158 6	164·3	173·9	175·3	...	...
Rape	9·17	32·1	61·31	75·36	78·09	92·55	101·4	110·1	128·9	132·6	139·6	145·2
Lard	11·3	14·52	49·58	71·46	86·36	101·2	116·8	128·5	138·0	147·3	148·7	155·0
Tallow	20·14	49·41	114·9	140·7	154·5	167·6	175·8	178·6	182·9	183·3	189·0	189·4
Castor	10·98	46·8	50·9	46·8	47·4	47·9	48·5	48·4	46·8	43·3	47·11	48·34

The acid values given in the preceding tables show that hydrolysis becomes very much slower when about 75 per cent. of the neutral fat has been hydrolysed. The fact that, under the conditions of the experiment, it was very difficult to keep up a thorough intermixture of fat and acidulated water, satisfactorily explains the slowing down of the reaction. It may be safely assumed that provided a thorough intermixture could be brought about, as is the case in an emulsion, hydrolysis would proceed much more rapidly. For the catalytic action of hydrochloric acid is exerted even at the ordinary temperature in course of time, as I have proved by some laboratory experiments.*

Much better results are obtained if *concentrated sulphuric acid* is used as the catalysing agent, for the reason, as I venture to think, a much better emulsion is produced.

To illustrate this by figures, I give in the following table a number of experiments which I have carried out :—

* Lewkowitsch, "Chemical Analysis and Technology of Oils, Fats, and Waxes," Macmillan and Co., London 1904, p. 43.

TABLE XII.

HYDROLYSIS OF TALLOW, CONTAINING 6·2 PER CENT. FREE FATTY ACIDS, WITH 4 PER CENT. OF SULPHURIC ACID OF VARYING STRENGTH (Lewkowitsch).

Acid containing per cent. SO_4H_2.	Per cent. Fatty Acids. After steaming for hours																					
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
98	42·1	65·1	79·3	83·7	88·6	91·7	91·7	92·3	93·0	92·3	93·0	93·6	93·6	93·0	93·6	93·6						
90	37·2	47·7	57·6	65·1	72·5	76·0	80·0	81·8	83·6	86·2	88·0	86·8	88·6	88·6	89·0	90·5	90·5					
85	34·1	45·2	50·8	62·6	68·2	73·1	75·0	76·2	79·4	84·3	84·9	89·3	89·3	89·3	89·9	89·9	89·9					
80	31 6	45·2	57·6	65·1	73·1	75·4	79·3	80·6	83·7	85·5	87·4	88·6	89·0	89·9	89·9	89·9						
70	15·5	16·7	17·9	18·3	18·6	20·3	24·8	26·5	28·5	31·0	32·6	34·7	35·4	37·0	39·0	40·1	42·7	45·2	46·5	47·7	47·7	47·7
60	6·2	6·2	6·2	6·2																		
50	6·2	6·2	6·2	6·2	6·8																	

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A still better emulsion is produced when Twitchell's reagent (the "sulpho-aromatic" compound prepared by allowing an excess of sulphuric acid to act on a solution of oleic acid in aromatic hydrocarbons) is used. By adding 1 to 2½ per cent. of this reagent to a fat practically complete hydrolysis will be reached on heating the fat in a current of steam, especially in the presence of a few per cent. of free fatty acids, which have been found to influence favourably the starting of hydrolysis.

This is shown by a number of experiments I have carried out. The results are reproduced in Table XIII.

I have endeavoured to show that the chemical reagents considered hitherto act as accelerators, and I have laid stress on the emulsifying action produced by them.

Now, the most thorough emulsion is obtained by the aid of *ferments*. Hence the correctness of the views which I have expounded here would seem to be convincingly demonstrated if ferments did possess the power of hydrolysing oils and fats. This is, indeed, the case.

One of the ferments which effects hydrolysis of fats in our own internal economy, *i.e.*, in the digesting process of fats, is "steapsin." In a number of experiments I made in collaboration with Dr. Macleod I have been able to show that the "steapsin" obtained from the pancreas of the pig is a comparatively powerful fat-hydrolysing ferment. This is demonstrated by the numbers given in Table XIV.*

More rapidly is hydrolysis brought about by the ferment contained in castor seed and a number of other plant seeds. In Table XV. I have collated a number of experiments published by Connstein, Hoyer, and Warten-

* Compare Lewkowitsch and Macleod, "Proceeding Royal Society," 1904, p. 31.

TABLE XIII.—Hydrolysis of Oils and Fats by means of Twitchell's Reagent (Lewkowitsch). 100 grms. of Oil or Fat, steamed up with 1 per cent. of the Sulpho-aromatic Compound in open flasks.

Oil or Fat.	Original Acid Value.	Acid Value after															
		2 hrs.	7 hrs.	9 hrs.	12 hrs.	14 hrs.	16 hrs.	18 hrs.	20 hrs.	22 hrs.	24 hrs.	26 hrs.	28 hrs.	30 hrs.	32 hrs.	34 hrs.	36 hrs.
Cotton seed ...	5·67	8·75	61·28	99·8	129·4	137·6	148·7	150·1	155·9	157·9	161·4	164·5	165·2	166·3	167·0	168·4	168·9
Whale ..	6·01	14·99	48·69	63·72	72·42	80·8	84·31	85·82	89·68	90·71	91·67	91·67	91·7	94·69	97·88	98·07	98·9
Rape	2·16	8·4	23·24	30·59	44·26	50·57	53·6	55·4	56·58	56·72	57·91	59·58	60·6	61·46	61·61	61·87	62·3
Lard	2·6	11·37	38·66	58·73	82·42	90·81	98·49	107·3	107·9	109·0	110·5	112·0	115·2	118·3	118·6	119·1	120·2
Tallow ...	11·15	15·03	25·68	43·44	49·39	50·11	52·03	53·1	53·85	55·6	57·11	59·82	60·23	63·95	66·2	67·3	68·5
Cocoa nut	18·75	114·0	221·4	232·9	233·2	236·0	236·2	237·2	237·9	238·9	239·5	239·8	239·8	240·6	240·9	241·0	241·2

TABLE XIV.—Hydrolysis of Glycerides with the aid of Steapsin Preparations (Lewkowitsch and Macleod).

Preparation.	Cubic Centimetres of Preparation per 100 Grams of Cotton Seed Oil or Lard.	Date on which started.	Added to Emulsion.		Per Cent. of Free Fatty Acids formed.					
			Acid.	Alkali.	Feb. 23	Mar. 2	Mar. 9	Mar. 16	Apr. 16	May 1
Cotton Seed Oil.										
1	20	19/2/03	0	0	22·9	...	43·3	48·4	80·6	...
1	30	19/2/03	0	0	32·8	...	49·9	60·45	86·7	...
1	25	19/2/03	0·5 c.c. of 2 per cent. acetic acid	0	10·22	26·4	41·04	48·8	74·7	...
1	30	19/2/03	0	0·5 c.c. 1/10 norm. NaOH	31·25	39·5	55·4	63·1	...	...
2	30	5/3/03	0	0	...	...	37·1	44·3	68·3	70·1
2	50	5/3/03	0	0	...	...	32·7	46·4	71·5	83·1
2	60	5/3/03	0	0	...	...	31·03	46·3	60·8	79·5
2	60	5/3/03	0·5 c.c. of 2 per cent acetic acid	0	...	...	30·4	45·2	65·3	73·1
2	60	5/3/03	0	0·5 c.c. 1/10 norm. NaOH	...	...	36·5	44·9	66·4	73·3
2	30	5 3/03	0	1 c.c. 1/10 norm. NaOH	...	...	31·4	43·8	74·1	74·1
2	50	5/3/03	1 c.c. of 2 per cent. acetic acid	0	...	...	37·66	44·5	65·2	77·1
Lard.										
2	50	5/3/03	0	0·5 c.c. 1/10 norm. NaOH	...	...	8·98	9·2	29·9	46·7
2	80	5/3/03	0	1 c.c. 1/10 norm. NaOH	...	...	12·2	14·4	20·7	22·1

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burg, which prove the feasibility of hydrolysing oils and fats by means of water if its action be assisted by the ferment contained in castor seed, and a small quantity of dilute acid be admixed as an additional accelerator.

Another class of accelerating agents, employed in practice on a very large scale, are *basic materials*, such as calcium oxide, magnesium oxide, and especially the caustic alkalis.

Now, if the view that the bases act as accelerating agents (in other words as catalysts) be correct, then it should not be imperative that the bases be present in at least molecular proportion to the fatty acids which will be liberated when the hydrolysis becomes complete. The greater the amount of the bases present, the more rapidly should the resolution of the glycerides into their component parts take place, and the greater should be the amount of salts of the fatty acids formed; but a deficiency in the amount of the bases required to neutralise all the fatty acids obtainable by complete hydrolysis should not preclude the completion of the hydrolysis.

Since the rapidity of saponification stands in direct ratio to the quantity of the bases, it will be possible, by using an excess of bases, to lower the temperature otherwise required for effecting hydrolysis, and to shorten the time within which it is practically completed. These points are clearly brought out in the technical process of saponification by means of lime. The quantity of lime requisite for the neutralisation of the fatty acids produced on completely hydrolysing a glyceride can be calculated from the following summarising equation:—

$$2\,C_3H_5\begin{matrix}O.R\\O.R\\O.R\end{matrix} + 3\,Ca(OH)_2 = 2\,C_3H_5\begin{matrix}O.H\\O.H\\O.H\end{matrix} + 3\,Ca(OR)_2$$

The amount of caustic lime—CaO—required for a triglyceride having the mean molecular weight 860, is 9·7 per cent., but even prolonged boiling with steam in an open vessel with this amount of lime will not lead to complete saponification. Unless the proportion of caustic lime be raised to 12-14 per

TABLE XV.—Hydrolysis of Oils and Fats by means of the Castor Seed Ferment.

Oil or Fat.	Grms.	Castor Seed.		Fatty Acids formed. Per cent.	After Hours.	Temperature.	Acid.
		Raw.	Extracted.				
		Grms.	Grms.			°C.	Grms. $\frac{n}{10}SO_4H_2$
Tallow	6·5	5	..	72	19	35	4 „ „
Bone fat	6·5	5	..	81	19	35	4 „ „
Cotton seed oil	6·5	5	..	84	19	35	4 „ „
Palm oil	6·5	5	..	87	19	35	4 „ „
Rape oil	6·5	5	..	84	19	35	4 „ „
Palm nut oil	16·5	5	..	76·6	20	Ordinary	8 „ „
Arachis oil	25	..	1·3	100	96	„	5 „ „
Rape oil	25	..	..	100	96	„	5 „ „
Poppy seed oil	25	..	..	100	96	„	5 „ „
Linseed oil	50	..	5	83	24	„	10 „ „
Blubber oil (I.)	50	..	5	76	24	„	10 „ „
„ „ (II.)	50	..	5	84	24	„	10 „ „
Olive oil	50	..	5	86	24	„	10 „ „
Sesamé oil	50	..	5	85	24	„	10 „ „
Almond oil	50	..	5	90	24	„	10 „ „
Cacao butter	50	..	5	92	24	„	10 „ „
Palm oil	75	..	7·5	77	6	„	15 „ „
„ „	75	..	7·5	96	22	„	15 „ „
Cotton seed oil	75	..	1·5	82	44	„	15 „ „
„ „	100	..	5	87	44	„	10 „ „
„ „	75	..	7·5	79	24	„	15 „ „
Triolein	10	..	..	50·6	24		
Triacetin	10	..	0·5	0·4	24		2 „ „
Tributyrin	10	..	..	9·5	24		

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cent., the hydrolysis of the glyceride cannot be brought to an end in an open vessel, *i.e.*, at a temperature of 100-105° C. If, however, the temperature be raised (as is done on a large scale by treating fats with milk of lime in an autoclave under pressure), the proportion of caustic lime can be greatly reduced until, at a pressure of 12 atmospheres corresponding to a temperature of 220° C., even 1 per cent. of lime suffices to effect complete hydrolysis. Although the glyceride is completely hydrolysed, yet only so much of the fatty acid is neutralised by lime, *i.e.*, converted into lime soap, as is chemically equivalent to the quantity of lime employed.

The same considerations—*mutatis mutandis*—hold good if caustic alkalis are used as accelerators. In the last case, hydrolysis proceeds much more rapidly, inasmuch as, in contradistinction to the process of hydrolysis assisted by lime, a water-soluble soap is formed, which helps to emulsify the fat.

In the next lecture we shall see how far the practice of manufacturing processes bears out the correctness of these theoretical considerations.

Lecture IV.—Delivered February 15, 1904.

In the last lecture we have dealt with the theory underlying the hydrolysis of oils and fats, and I there advanced the view that the splitting up of the fat molecule into its constituents is effected solely by means of water assisted by certain accelerators. To-night we shall descend from the blue sky of theory to the solid ground of fact, and consider how far these theoretical views are borne out in practice by those manfacturing processes that are in vogue at present.

Candle Industry.

I have shown that water alone, at high temperatures, is capable of effecting hydrolysis, according to the equation :—

$$\begin{matrix} O.R \\ C_3H_5\ O.R \\ O.R \end{matrix} + 3\ H.OH = \begin{matrix} O.H \\ C_3H_5\ O.H \\ O.H \end{matrix} + 3\ R.OH$$

This reaction can be realised in practice, and has indeed been carried out on a large scale by heating fats with water at high temperatures. The first attempt to work such a process on an industrial scale was made 50 years ago by R. A. Tilghmann, whose method consisted in forcing an emulsion of fat and water through an iron tube heated in a furnace to a temperature of about 330° C. This process, the plant for which I show in a lantern slide, possesses only historical interest to-day, for it was soon abandoned on account of the incomplete saponification and of the destruction of fatty material at the high temperature.

Since the employment of free fire involves the danger of burning the fat, the efforts of later inventors have been directed to carrying out the hydrolysis by means of water in an autoclave. These efforts have met with greater success. From the following table (Table XVI.), it will be gathered that, with the increase of pressure under which water acts on the glycerides, or, in other words, with the increase of temperature of the heating steam, the rate at which hydrolysis takes place is much increased. In practice, steam at a pressure of 15 atmospheres = about 220 lbs. per square inch (corresponding to a temperature of about 200° C.) is capable of effecting hydrolysis to a very high extent.

An apparatus worked on a practical scale is Hughes' apparatus (Fig. 10), which I saw in operation in a Paris factory fifteen years ago. The fat is charged into the autoclave A, about 30 per cent. of water are added, and steam, generated in a multi-tubular boiler at a pressure sufficiently high to keep up a working pressure of 15 atmospheres in the apparatus, is sent into the autoclave. The steam is finely divided into streamlets by a distributor similar to the one shown in Fig. 14. In order to provide additional security, beyond that afforded by the safety valve, against explosion, and in order thoroughly to agitate the mass, a small amount of steam is allowed to escape continuously through the pipe E, which thus serves as an extra safety valve. The escaping steam is made use of for the concentration of a glycerin solution charged (through pipe G),

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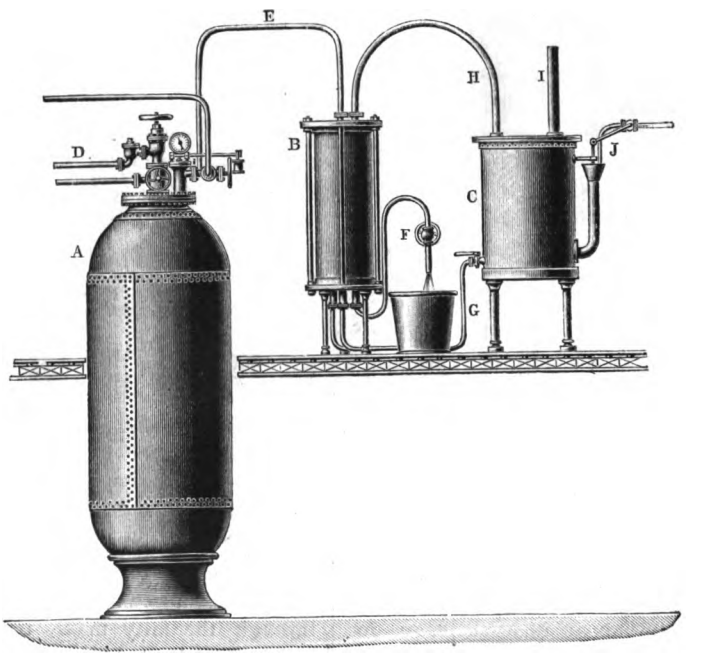
TABLE XVI.—Aqueous Saponification of Neutral Fats under Pressure.

30 grms. of Oil or Fat and 300 grms. of Water.

Kind of Oil or Fat.	At a pressure of Seven Atmospheres. Acid values after				At a pressure of Fifteen Atmospheres. Acid values after			
	2 hrs.	4 hrs.	6 hrs.	8 hrs.	1½ hrs.	2 hrs.	4 hrs.	6 hrs.
Cocoanut Oil	0·1	0·3	0·5	0·9	78·6	90·2	123·9	185·5
Japan Wax	4·8	5·3	9·4	13·1	..	12·3	32·5	46·1
Tallow	17·5	37·3	67·3	84·8	..	62·3	106·3	155·8
Pressed Tallow..	15·3	38·3	65·5	81·6	..	60·4	98·7	160·3
Cocao Butter	12·3	24·5	41·1	62·6	..	34·5	76·1	160·5
Olive Oil	15·1	32·1	53·0	71·4	..	66·5	114·5	159·5
Sesamé Oil	14·3	31·1	56·2	76·0	..	61·7	108·4	153·7
Cotton Seed Oil	10·0	23·2	36·3	51·7	..	42·2	80·2	128·6
Linseed Oil	11·4	21·1	43·3	56·1	..	38·1	78·5	130·5

Fig. 10.



into vessel B, in which is enclosed a heating coil connected with E; the condensed water escapes through valve F, which latter acts as a kind of steam trap. The steam evolved from the glycerin solution in B, serves to pre-heat a dilute glycerin solution fed into vessel C at J. In consequence of the high temperature, the material in the autoclave becomes seriously discoloured, so that the fatty acids must be chiefly worked up by the "mixed process" (see below). Moreover, since the hydrolysis of the fat does not reach so high a percentage as is the case in the processes of saponification with the assistance of bases, a small percentage of lime, about 1 per cent., is usually added to the mass into the autoclave. Hence, practically speaking, this method approaches very nearly the one applied in the lime saponification process.

The saponification is not only accelerated by the high temperature, but also by the thorough emulsion that is produced by violent agitation. In order to produce a still more thorough intermixture between fat and

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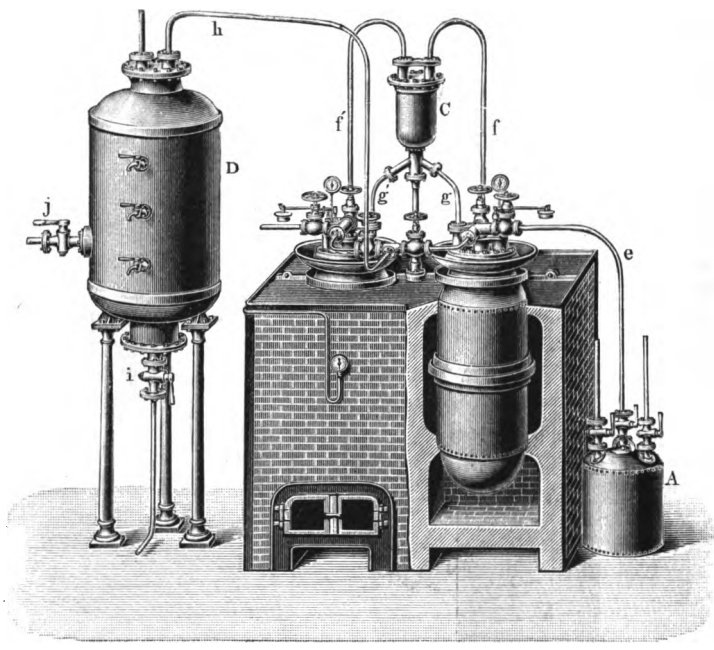
water, Michel designed the apparatus shown in Fig. 11. A pair of autoclaves is worked conjointly. They are charged through the pressure vessel, A, and pipe *e* with fat and water. The autoclaves are heated by fire, and as the pressure rises the contents of the autoclaves are forced up through the tubes, *f f'*, which reach almost to the bottom of the autoclaves, into the top of the mixing vessel C, whence the mass falls back again into the autoclaves. The mass, somewhat cooled in C, falls to the bottom of the autoclave through the hot mass therein, thus contributing to the steam stand in a definite relation to each other, it follows that high pressure steam may be replaced by superheated steam standing under ordinary pressure. Hence hydrolysis should become feasible by treating fats with superheated steam at a sufficiently high temperature. A process based on the hydrolysis by means of steam under the ordinary pressure was patented as early as the year 1825 (Eng. Pat. No. 5183, 1825), but it did not gain practical importance until Wilson and Payne took their patent for "Improvements in distilling fatty and oily matters" (Eng. Pat. No. 1624, 1854).

FIG. 11.



thorough intermixture of fat and water. This play repeats itself, whilst the pressure on the autoclaves is kept up at 15 atmospheres for eight hours. The hydrolysed mass is then forced through pipe *h* into the vessel D, in which separation into two layers—an upper layer of fatty acids and a lower layer of glycerin water ("sweet water")—takes place. The heating of the autoclave by direct fire is, however, a serious drawback of the process, as it may possibly lead to burning of the fat. Therefore, Michel's method is less acceptable than Hughes'. The autoclaves were shown at the Paris Exhibition of 1889, but, as far as I am aware, the process has not been adopted in Europe.

Since the pressure and the temperature of In their process, glycerides were heated in a still, whilst superheated steam was sent through the fatty mass, the temperature of which was kept between 550° and 600° F. The products of hydrolysis, viz., the fatty acids and glycerol (glycerin), were carried over by the water vapours. The apparatus employed was similar to the one illustrated in Fig. 13. (p. 41). Although this process is stated to have been worked for a number of years, it has been abandoned, since considerable quantities of fatty matter underwent destruction. I endeavoured (Eng. Pat. No. 5985, 1888) to render practicable this mode of hydrolysing fats by heating them in a current of superheated steam *in vacuo*. Also this process proved unremunerative, and was therefore abandoned.

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In the processes described hitherto the intermixture between fat and water is perhaps not a sufficiently intimate one; hence a somewhat long time is required for the completion of the reaction. If a thorough emulsion could be kept up at that high temperature, it should be feasible to carry out the process in a shorter time. As an example of the beneficial effect of a thorough emulsion, I may point to that produced by ferments, especially by castor seed ferments. The results obtained in a series of laboratory experiments with the latter ferment have been given already in Table No. XIV. (Lecture III. p. 34.). These results appeared sufficiently encouraging to propose the process as a manufacturing operation. This is conducted as follows:—The castor seeds, either decorticated or in their original state, are ground up to a fine pulp, and mixed with about 50 per cent. of water, calculated on the quantity of fat to be hydrolysed; this is then thoroughly intermixed with the oil or fat. The emulsion is allowed to stand about two days when the bulk of the fat is found to have been hydrolysed. I show here the product obtained in this manner from cotton seed oil. In this special case hydrolysis amounting to as much as 90 per cent. has been reached. Another example illustrating this process is the product obtained from tallow; here hydrolysis has taken place to the extent of about 80 per cent. only. Evidently tallow does not lend itself to this process as readily as cotton seed oil.

Since practically complete hydrolysis, such as is obtained in the apparatus shown in the last figures is not obtained by this ferment process, it must be considered as useless to the candle-maker, who requires free fatty acids (as we shall see later on). Still, I have particularly mentioned this process as it affords, in my opinion, the best illustration of the view which I have so frequently insisted upon, that water alone, if properly assisted by some accelerator, is capable of saponifying oils and fats.

A less thorough emulsion is effected by means of Twitchell's reagent. The mode of preparing this reagent has been already described in the last lecture, and its action on oils and fats has been illustrated by Table No. XIII., p. 34.

I have experimented with a number of "Twitchell's reagents," in which benzene was replaced by naphthalene, anthracene, and phenanthrene. I have found that the best results were obtained by using naphthalene, as can be readily seen from the following tables.

On saponifying on the large scale, it is necessary to start with a fat containing at the outset a few per cent. of free fatty acids, as without this expedient the reaction does not set in rapidly. This process has been introduced in several works in the United States, as it is specially suitable for low class material, which would be too expensive to work up in an autoclave on account of the high percentage of free fatty acids. Moreover, the high percentage of free fatty acids ensures the ready starting of the hydrolysis.

This process differs favourably from the last-mentioned one, in that it is suitable for

TABLE XVII.—Hydrolysis of Cotton Seed Oil by means of 1 per cent. of Sulphostearo-aromatic. Compounds (Lewkowitsch).

(a) Neutral Oil.

Sulphostearo-aromatic compound of	Original Acid Value.	6½ hrs.	13 hrs.	19½ hrs.	26 hrs.	32½ hrs.	39 hrs.	45½ hrs.
Naphthalene	1·22	146·7	190·7	201·4	211·4	..	..	..
Anthracene	1·22	2·5	21·8	76·3	170·7	186·5	190·7	..
Phenanthrene	1·22	45·7	125·7	177·7	183·6	194 1	201·2	..

(b) Oil containing Free Fatty Acids.

Sulphostearo-aromatic compound of	Original Acid Value.	6½ hrs.	13 hrs.	19½ hrs.	26 hrs.	32½ hrs.	39 hrs.	45½ hrs.
Naphthalene	8·3	30·9	194·1	216·9	210·7	..	..	..
Anthracene	8·3	15·01	60·5	112·4	147·2	148·2	189·8	202·8
Phenanthrene	8·3	42·3	159 9	156·4	181·6	184·2	204·2	204 2

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the candlemaker, as practically complete saponification is reached in the same or even a shorter time than in the ferment process. I show here a sample of tallow fatty acids prepared by the Twitchell process. They are somewhat dark in colour; this accounts for the fact that the fatty acids are not suitable for soap making, at any rate not in this country.

The Twitchell process seems to form a kind of intermediate link between hydrolysis by means of water alone and hydrolysis effected with the assistance of concentrated sulphuric acid. The latter is the well-known acid saponification process which has been practised for many years. I have shown by means of Table No. XII. (Lecture III., p. 33) how the hydrolysis (saponification) of tallow proceeds if 4 per cent. of concentrated sulphuric acid are employed as an accelerating (emulsifying) agent. This process is easily carried out on the large scale. The fat is freed from water by heating it to 120° C. and mixed with a few per cent. of sulphuric acid for a few minutes at 120° C. in a mixing machine such as is shown in Fig. 12; the whole mass is then run into boiling water and steamed for a certain number of hours, until complete decomposition of the intermediate product is effected. The nature of these intermediate products has not yet been completely investigated. They appear to consist of sulpho-compounds of fatty acids. Whilst the saturated acids, palmitic and stearic acid, are finally recovered, after steaming, as such, the liquid oleic acid is to some extent converted into solid products, so that the yield of candle material from a given fat, in consequence of the conversion of oleic acid into a solid material, is greater than the yield obtained by the saponification we shall consider presently.

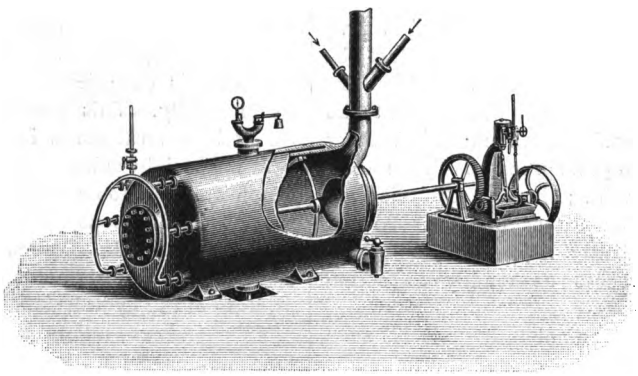
The progress of hydrolysis taking place in the course of steaming the mass is illustrated by the following table:—

TABLE XVIII.—TALLOW HYDROLYSED WITH 4 PER CENT. OF CONCENTRATED SULPHURIC ACID AT 120° C. (Lewkowitsch).

	Contained Free Fatty Acids. Per cent.
Sample taken after 1 hour's steaming	42·1
,, ,, 2 hours'	65·1
,, ,, 3 ,, ...	79·3
,, ,, 4 ,, ...	83·7
,, ,, 5 ,, ...	88·6
,, ,, 6 ,, ...	91·7
,, ,, 7 ,, ...	91·7
,, ,, 8 ,, ...	92·3
,, ,, 9 ,, ...	93·0

The product obtained by this process as illustrated here by several samples prepared from various materials, is somewhat dark,

FIG. 12.



but the colour is not of great importance to the candle maker, as he is able to purify the material cheaply, by distillation in a still such as is shown in Fig. 13. The acid-saponification process is especially suitable for working up low-class material, which contains little glycerin, as a certain amount of glycerin undergoes destruction. The loss of glycerin is, however, compensated for by the larger yield of candle material, as pointed out already.

In order to more fully understand this, let us consider tallow, which may be looked upon as consisting of palmitin, stearin, and olein, and let us assume that the yield obtainable from tallow by an autoclave process is 45 to 47 per cent. of palmitic and stearic acids, and 48 or 47 per cent. of oleic acid. The former 45 to 47 per cent. are useful as candle material, whereas the latter 48-47 per

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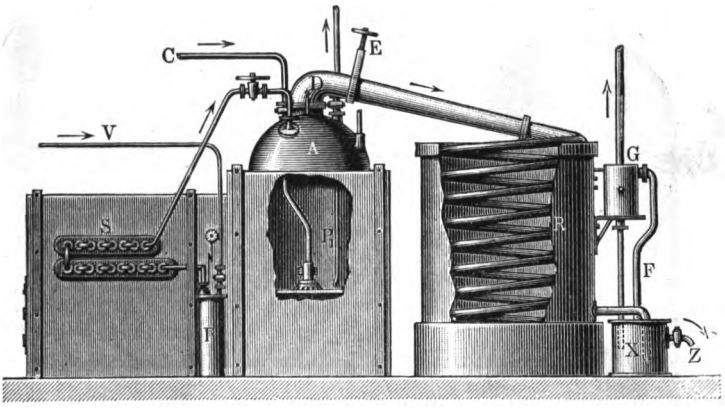
cent. are a by-product which must be disposed of in the best possible manner. Since, however, in the acid saponification process (as mentioned already) a portion of the oleic acid is converted into solid material useful for candle making, the candlemaker would obtain by the acid-saponification proce of tallow something like 63 per cent. of candle material, and only 30 per cent. of the less valuable oleic acid.

This explains why the acid saponification process finds wide application, especially so in the case of those fats which are impure and contain a large amount of free fatty acids, so that the yield of glycerin from them would in any case be much smaller than from fresh neutral fats.

actually practiced largely; it is known under the name "mixed process," and may be likened to the "huilerie mixte" we have considered in the first lecture under the production of olive oil. Thus, the mixed process consists in hydrolysing fats in an autoclave, removing all the glycerin formed, and treating the fatty acids with concentrated sulphuric acid so as to obtain the higher yield of 63 per cent. of candle material.

Since for a process of this kind the freshest neutral fats can be used, the hitherto described autoclave processes would appear to be too costly. The endeavour of the candlemaker has therefore been directed to accelerating the process of saponification by such catalysts as we have seen (in the third lecture) to be of

FIG. 13.



Since the yield of glycerin forms a very important item in the economics of any saponification process—especially so to the candlemaker — in contradistinction to the soapmaker—the efforts of the candlemaker have been directed to recovering the full amount of glycerin.

It has been shown that a certain amount of glycerin undergoes destruction in the acid-saponification process, so that even by working it most carefully loss must occur. If we consider that the action of sulphuric acid on oleic acid is practically the same as the action on olein, as regards the obtainment of a high yield of candle material, the most advantageous process would appear *a priori* to be some such one in which the full amount of glycerin is recovered—as in the autoclave processes considered above—and the concentrated sulphuric acid be allowed to act on the *free fatty acids*. A process of this kind is

assistance in the saponification in autoclaves, namely, basic substances. Since caustic alkalis are out of the question on account of their cost, the candlemaker uses lime, magnesia, and zinc oxide.

In the oldest process, the one proposed by de Milly, fats were saponified by means of 12–14 per cent. of lime in an open vat, so that the total amount of fatty acids was converted into lime soap. The latter was then decomposed by sulphuric acid in order to liberate the free fatty acids which form the candlemaker's raw material.

We have seen in the last lecture that by increasing the pressure under which hydrolysis is carried out, the proportion of the accelerator may be reduced. Indeed, this is done at present in the well-known process of the candlemaker, who hydrolyses the fats in an autoclave by means of 3 per cent. of lime, under a pressure of 8 atmospheres. The

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usual autoclaves are illustrated by Figs. 14 and 15. The autoclave, Fig. 14, consists of a cylindrical vessel made of copper, strong enough to withstand a working pressure of eight atmospheres, and provided with an internal steam pipe, which reaches the bottom of the vessel. In Fig. 14 the steam leaves at the bottom of the serrated cone, and is thus divided into a number of streamlets, which churn the mixture of fat and water into a thorough emulsion. The water and fat, in the proportion of 1 to 3 or 1 to 4, as also the lime, in the form of milk of lime, are fed

FIG. 14.

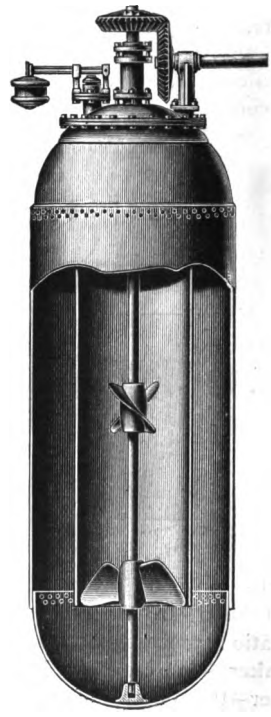
through the funnel-shaped vessel at the side of the autoclave. In the other form of autoclave illustrated by Fig. 15, the agitation effected by steam is assisted by a mechanical stirring arrangement.

A horizontal form of autoclave, fitted with a stirring arrangement of a different kind is illustrated by Fig. 16. Since the cylindrical autoclaves are liable to be bulged out by high pressure, they would at last, if bulging took place progressively and in a regular manner, assume the shape of a sphere. Hence, also spherical autoclaves are in vogue. An autoclave of this kind, provided with a stirring arrangement, is shown in Fig. 17.

In the processes considered here the hydrolysis reaches as high a figure as 98 or 9[illegible] per cent.

When the saponification is deemed complete, the saponified mass is allowed to rest in the autoclave until it has separated into two layers—a lower layer of glycerin water ("sweet water"), and an upper layer of fatty acids, containing so much lime soap as corresponds to the lime introduced into the autoclave. These two layers are either pumped separately into store vats, or in order to save time, the whole mass may be pumped into a

FIG. 15.



settling tank, where the separation into the two layers takes place. The further working up of the glycerin water will be considered below.

The fatty material consists of a mixture of solid acids and oleic acid as described already. If best materials have been used, then it is not advisable to acidify the total fatty acids, as obviously the solid acids would merely be carried through the process as so much inert material, and thus increase the cost of the process. In such a case, the oleic acid is separated from the mixed fatty acids by pressure. This is carried out in the following manner;—The mixed

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fatty acids after being thoroughly freed from mineral acid, are run into shallow trays arranged in tiers, in which the fatty acids are allowed to crystallise. The temperature at which the crystallisation takes place is carefully regulated, so as to obtain well formed crystals of stearic and palmitic acids embedded in the mother liquor of oleic acid. If the fatty acids are cooled too rapidly, they solidify to an amorphous mass, from which it is extremely difficult satisfactorily to express the oleic acid. The solidified mass is taken out of the trays and pressed, at first at the ordinary temperature in a cold press, such as shown in Fig. 18. The bulk of the oleic acid —"red oil"—is thereby removed. The hard cakes still contain too much oleic acid, and are therefore expressed for the second time, at a somewhat higher temperature, in a hot press (Fig. 19), the cakes being placed in bags of horsehair or other suitable material between two press plates, which are heated by live steam. In the figure shown the steam is supplied from above; but since the stuffing-boxes, owing to the wear and tear to which they are subjected, require frequent renewing, the steam is supplied in more modern presses from below.

Fig. 16.

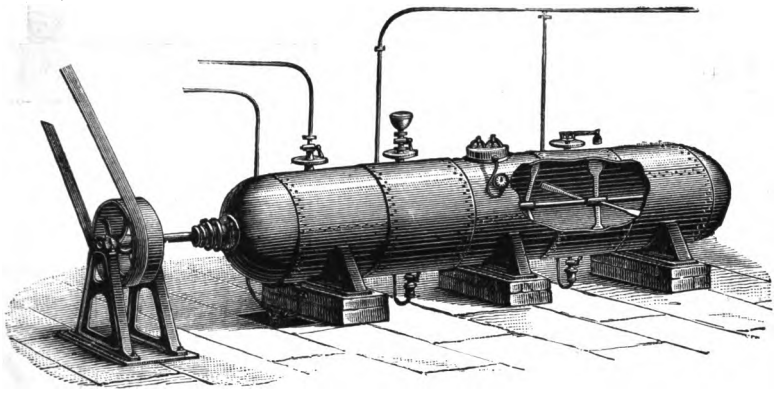
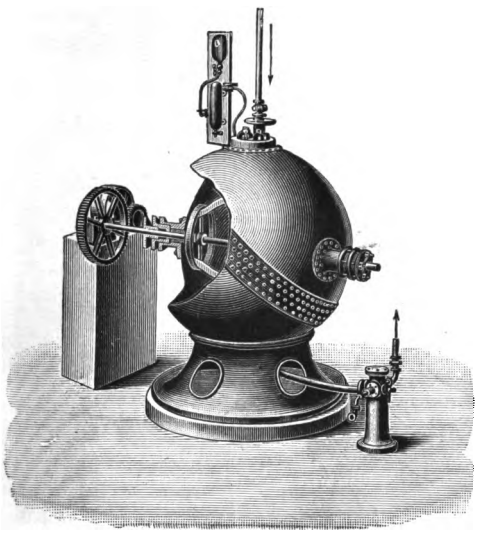


Fig. 17.



The cakes are allowed to stand under pressure in the hot until a sufficient amount of oleic acid has been expressed to leave the cakes white, ready to be melted (after a further purification if required), and to be moulded into candles. The oleic acid which runs from the hot-pressed cakes contains a considerable amount of solid acids—"stearine." These are recovered on a large scale, either by admixing the expressed material with the original fatty acids, or by treating it together with the "red oil" in a refrigerating plant, where the oleic acid is cooled in large tanks either by means of cold brine, or a calcium chloride solution sent through a row of coils in the tank.

A more rapid method of cooling consists in allowing the oleic acid to run over a refrigerating wheel—Petit's wheel (Fig. 20). This is partly shown in section. The cooled brine enters at c, runs along the circumference of the wheel, and leaves at the opposite side. The oleine is fed into trough *f*, into which the refrigerating wheel dips, carrying with it upwards a thin film of oleic acid, which is thus rapidly cooled, and deposits crystals of "stearine." The crystalline mass on reaching the scraper h, is scraped off, and the sludgy

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FIG. 18.

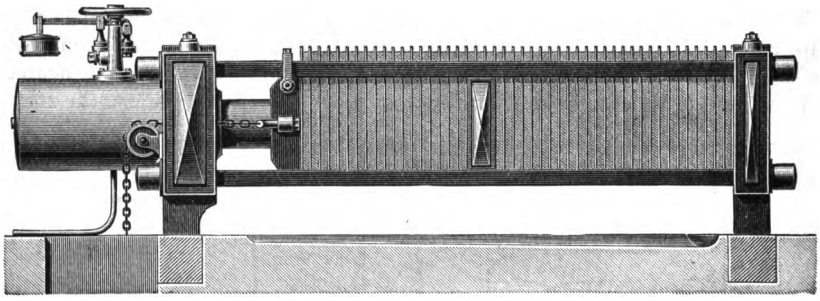


FIG. 19.

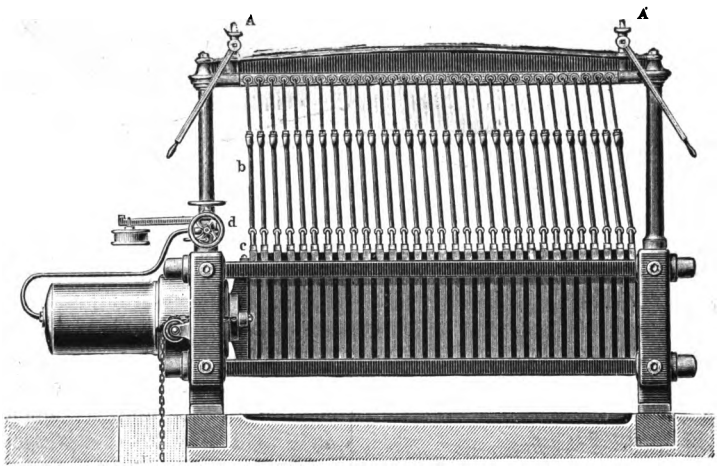
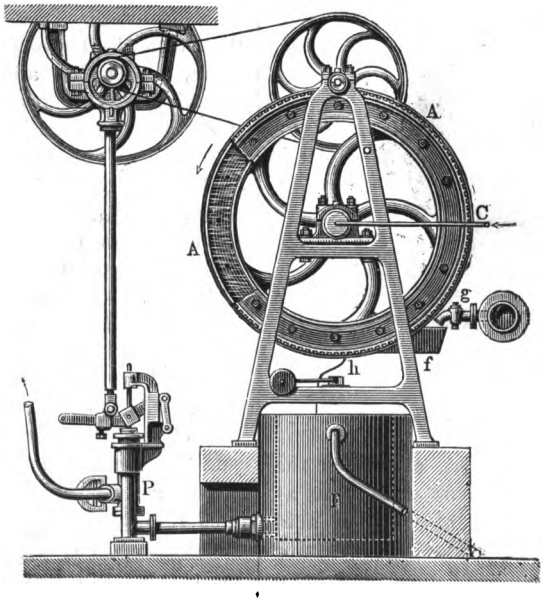


FIG. 20.



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mass collected in the cooled vessel F, from which it is pumped through pump P into a filter press. The crystals are then introduced as an intermediate product at a suitable stage of the process into the crude candle material. The oleic acid may be converted as far as possible into solid candle material in the manner shown above.

If the raw candle material charged into the autoclave be of inferior quality and incapable of yielding white stearine by expression, then the total mass from the autoclave is acidified, *i.e.*, treated in the manner described already under the acid saponification process, and separated after distillation into stearine and oleic acid.

The hot pressed stearine is then ready to be moulded into candles. This is done in well-known machines, like that shown in the later part of the lecture (Fig. 23), with that difference that in the latter machine the bobbins on which the wicks are wound in a candle-moulding machine are left out.

The moulded candles, before being placed on the market, are polished, washed, dried, and finally branded, if required, in a set of machines which I show in a series of lantern slides.

Owing to the expensiveness of stearine, paraffin wax is being largely used in admixture with stearine. A series of cast blocks of candle materials representing mixtures of "stearine" and paraffin wax in various proportions are exhibited on the table here.

Soap Industry.

Whereas the chief care of the candle-maker is directed to obtain as much free fatty acid, and especially solid acids, as possible, the main object of the soapmaker is to obtain *all* the fatty acids in the form of soap, *i.e.*, in the form of sodium or potassium salts of fatty acids. Hence, he will, when hydrolysing his fats, use as an accelerator only such a base as will yield him straightway hard soaps—sodium salts, or soft soaps—potassium salts. In other words, the soapmaker hydrolyses (saponifies) his oils and fats with caustic soda or with caustic potash, in an open pan, and converts, by the well-known suitable treatment, the soda salts into a mass which on cooling in large frames—soap frames (a model of which I show here)—solidifies, in the course of a few days, to a solid block. The sides of the soap frames are then removed, and the rectangular block of soap left is first cut into slabs of the required thickness, either by hand, or by a machine such as shown in Fig. 21, and then into tablets by a machine such as shown in Fig. 22.

As the solidification of the soap requires several days, attempts have not been wanting to shorten the time required for cooling from the finishing operation in the soap pan to the conversion of the solidified soap into the marketable bar or cake.

I have attempted to effect this by sending the soap through a long worm, cooled artificially*, but the soap so obtained represented an unsaleable mass, owing to the crystalline structure of the soap having been destroyed. Another attempt to effect this rapid solidification of the hot soap mass was made by moulding the soap in the same manner as candles are moulded.† The machine used for this purpose (Fig. 23), is fashioned after the well-known candle moulding machine. It was chiefly intended for the manufacture of toilet soaps, in which the crystalline structure, so much valued in household soap, is destroyed. The hot soap mass was run into the several moulds shown in the figure, and after suitable cooling, the solidified soap was expelled in the same manner as moulded candles are forced out.

This machine proved unsuitable for household soaps, but the idea underlying the construction of this machine has been recently taken up and patented by Schnetzer. At present nothing can be said as to the success obtained by his plant. Another attempt to shorten the time required for solidification has been made by Klumpp, whose press is best described as being fashioned after a copying press, the sides of which are completely closed. The hot soap is run into the press, and when full, the soap is cooled rapidly and compressed, so that the soap bars are immediately ready for being divided into tablets. A combination of the principles embodied in these two patents may be said to be contained in Schrauth's patent.

We have learned from the fundamental equation representing the hydrolysis of fats (Lecture III., Equation 1, p. 27), that glycerin results as the second product. The candlemaker obtains the glycerin in an aqueous solution. The soapmaker, however, who produces hard soaps in an open pan, obtains his glycerin in a solution containing a large amount of salt,

* Lewkowitsch, "Problems in the Fat Industry," *Journ. Soc. Chem. Ind.*, 1903, 597.

† English Patent, No. 4581, 1893.

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alkali, and impurities, but so small an amount of glycerin that up till about two decades ago the soapmaker's so-called "spent lyes" were run away into the nearest watercourse.

Although it was well known that immense quantities were wasted in this fashion, still, the great difficulties that beset the recovery of glycerin from the spent soap lyes militated against their being worked up on a commercial basis. But since the employment of nitroglycerin in the manufacture of dynamite, blasting gelatine, and a host of other modern high explosives, created an enormous demand for glycerin, the recovery of glycerin from soap lyes has been taken up energetically, with the result that practically every large soapmaker in this country recovers the glycerin from the spent lyes.

It may as well be pointed out that this country has taken a leading part in this industry, and was practically the first to recover glycerin from the soap lyes on a large scale. America and France have followed suit, and the most prominent soapmakers there now produce glycerin from their lyes.

In other countries, where the soapmaking ndustry has not yet reached the rank of the important chemical industry it really is, and where it is only slowly emerging from the stage of a house industry, the recovery of glycerin is still in its infancy. This is chiefly due to the fact that soapmaking is in the hands of many small makers, so that in a town of 10,000 inhabitants three or four soap makers will be found to supply the local demand.

The present flourishing state of the soap industry in this country, chiefly due to the profits resulting from the recovery of the glycerin, has latterly drawn the attention of technologists on the Continent to the method of obtaining the glycerin from the fats first, and then converting the fatty acids into soap. Theoretically considered, this seems the most natural process, and for the last 70 years this process has indeed been practised in a number of candle works. The oleic acid was there converted into soap by boiling with caustic soda, or more simply still with sodium carbonate, a process which, theoretically, is identical with that of neutralising, say, hydrochloric acid by sodium carbonate.

The products which the candlemaker thus obtained being dark, the soaps so produced were dark and of evil odour. This method has again been taken up lately on the Continent but in order to minimise the darkening effect which the fatty acids must suffer in an autoclave, the pressure was reduced, and thus a better looking product was obtained than from material autoclaved at the high temperature. This modification has, however, that important

FIG. 21.

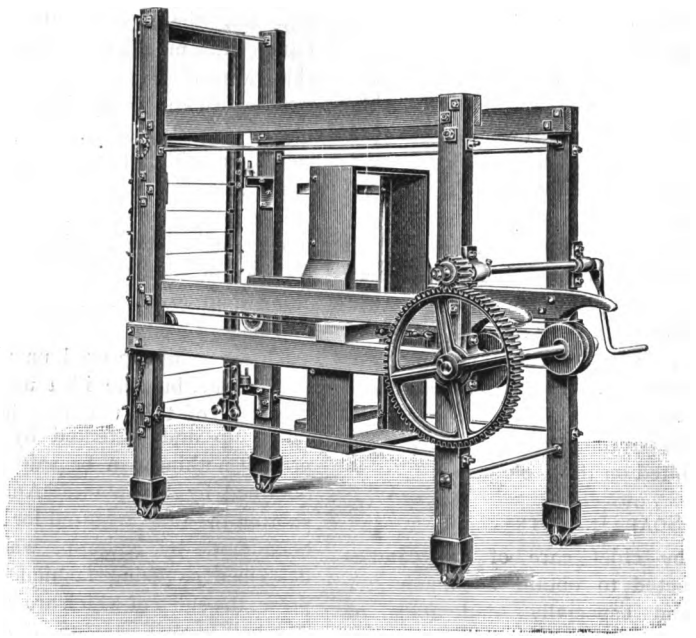

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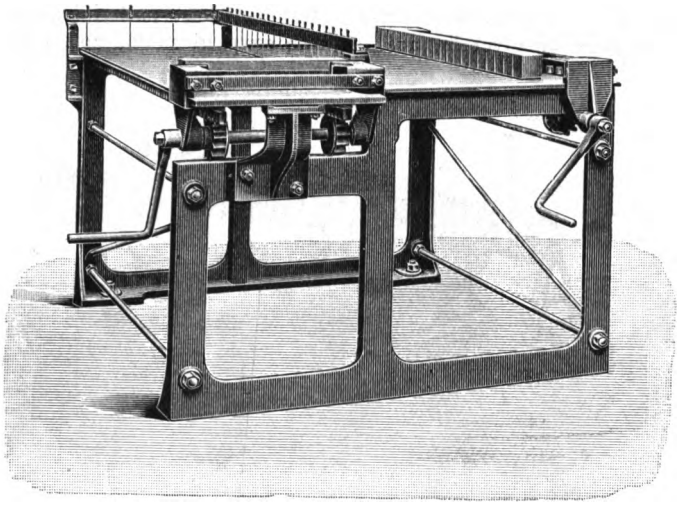
FIG. 22.



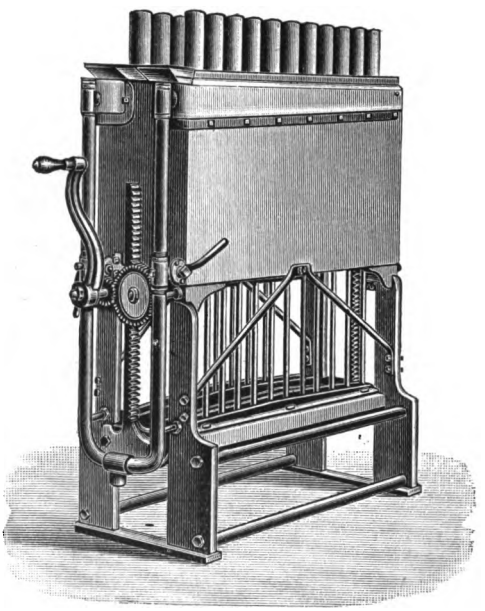
drawback that saponification cannot be carried on to the end, and products are obtained which contain 15 to 20 per cent. of unsaponified fat. The glycerin contained in this unsaponified portion of fat is irretrievably lost, as it does not pay to recover it from the lyes obtained in the soap pan.

These "improved" processes are being put on the market as new or "patented" processes with a great flourish of trumpets and an amount of advertising in the trade papers, which betrays too openly the interest that some makers of autoclaves have in pushing their wares. There are no less than about 40 processes on the market, each of which claims to work with an autoclave of its own, or, if you like, about 40 different autoclaves, each of which is worked with a "special process."

After what I have said before, I need not point out that these patents are valueless, and it is not a little amusing to see the travelling agents for these autoclaves on their visit to this country shake their heads mournfully over the backward state in which our chemical manufacturers in general, and our soapmakers in especial, are still found.

Of course, these methods have been tried long since in this country, and have been found wanting, as the soap so obtained is unquestionably darker and unsaleable, at any rate in this country, at its proper price. On the Continent these processes may commend themselves to some extent to those soapmakers, who have hitherto wasted their glycerin, and who are able to sell a soap at which an English housewife would look askance. But even on the Continent it is candidly being acknowledged that first-class soaps cannot be obtained by an autoclave process.

FIG. 23.



In the case of *soft* soap the glycerin has hitherto not been recovered, and it passes wholly into the soap. Although the soapmaker consequently loses the profit the glycerin might bring him, he has at least this advantage, that his soap is a readily saleable

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article, commending itself by its brilliancy and transparency.

Soft soaps made from autoclaved material, and therefore very poor in glycerin, are of

facturers, the greatest consumers of soft soap, will not accept a soft soap devoid of glycerin for their best materials, as the glycerin in the soap gives that soft feel and gloss which

FIG. 24.

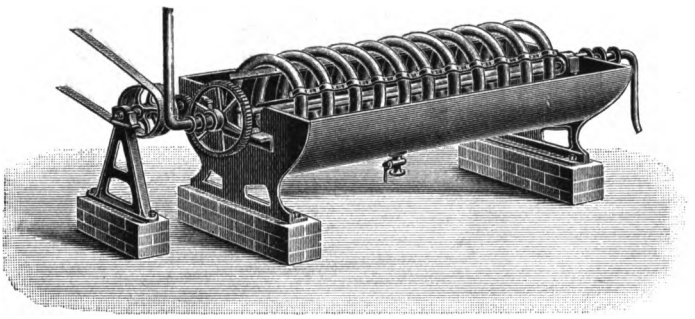
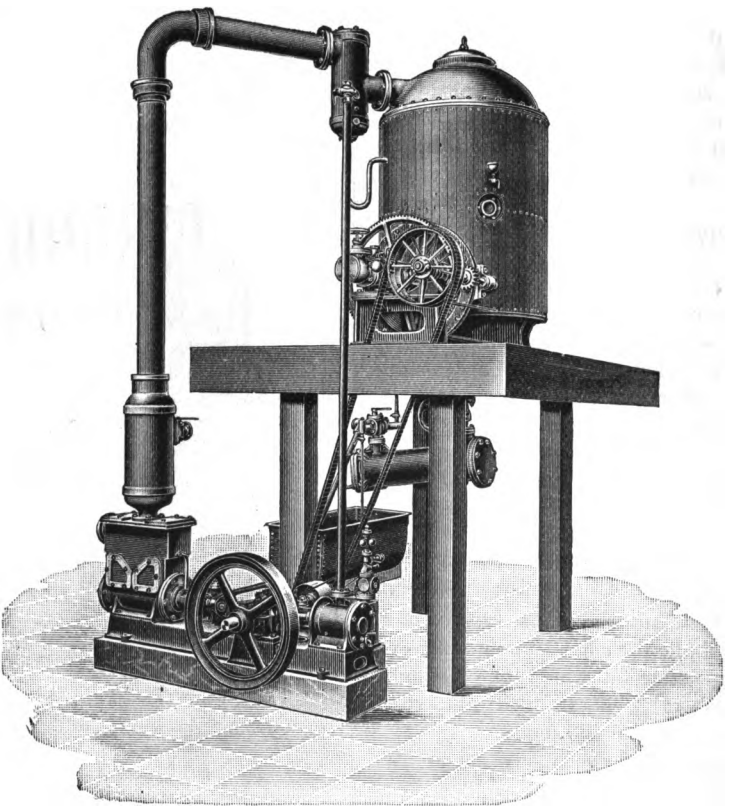


FIG. 25.



dark colour and of uninviting appearance. Besides, they will not, in the true sense of the word, hold water, which the soapmaker is always suspected (erroneously, I may add) by the public to make it his chief business to introduce into soap. Moreover, woollen manu-

are, *e.g.*, in cashmeres, the first recommendation to the buyer.

I am aware that in one or two establishments in this country the making of soft soaps from fatty acids is being carried out experimentally—for a good traveller will always b

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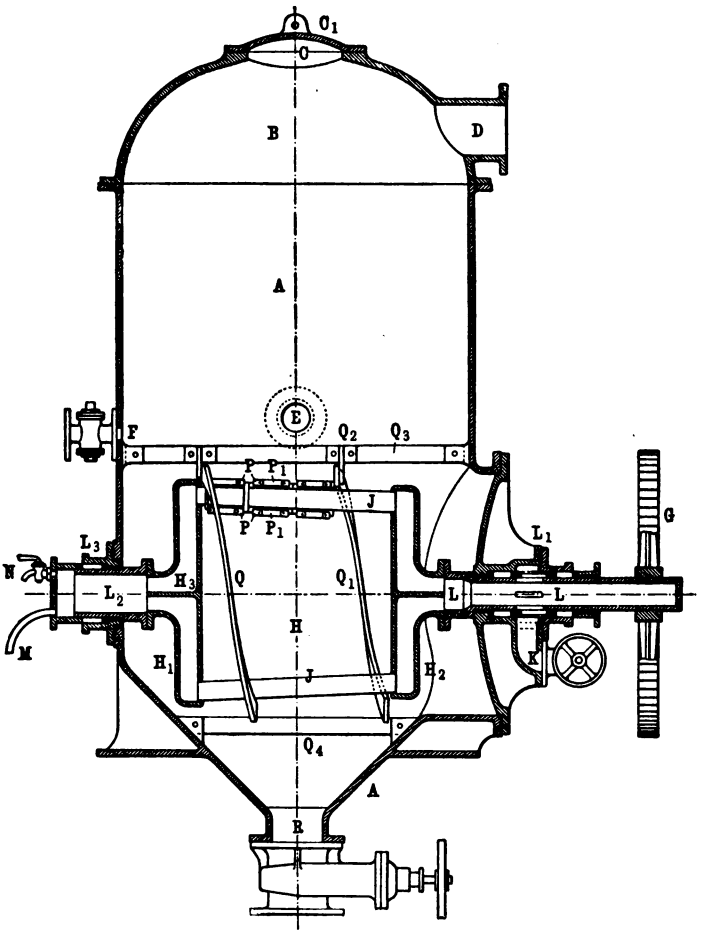
able to find one or two customers. The future must show how far the dark soaps produced there will be able to maintain themselves in the market.

Toilet soaps are prepared from "genuine" soaps made by the boiling process. As a preparatory process the bulk of the water must be removed. This is done by cutting the soap into fine shavings by means of a rotary cutting machine, and spreading the shavings on trays in a steam-heated chamber. In large establishments the shavings are carried on an endless band through the drying apparatus. The soaps lose thereby about 20 per cent. of water, and are then ready to be worked in a milling machine, between granite rollers, into fine shreds. At this stage of the operation colouring matter, as also perfumes and medicaments, are intermixed. The mass is repeatedly passed between the rollers until a uniform mass is obtained. The shredded soap is next transferred to a machine in which the shreds are compressed by means of a screw, and driven against a plate perforated with a number of small holes, so that the soap passes this part of the machine in the form of single thick threads. These are again compressed a a somewhat elevated temperature, so that the threads can coalesce and leave the machine in the shape of a continuous bar of soap. This bar is then cut up into small cakes, which are finally stamped, and then present the familiar form of the soap tablet.

FIG. 26.



Another kind of soaps that are coming very much to the front are *dry soaps*. They are prepared by grinding together hard soaps with sodium carbonate. The hard mass obtained thereby is broken up in a mill, and then reduced to fine powder in a disintegrator,

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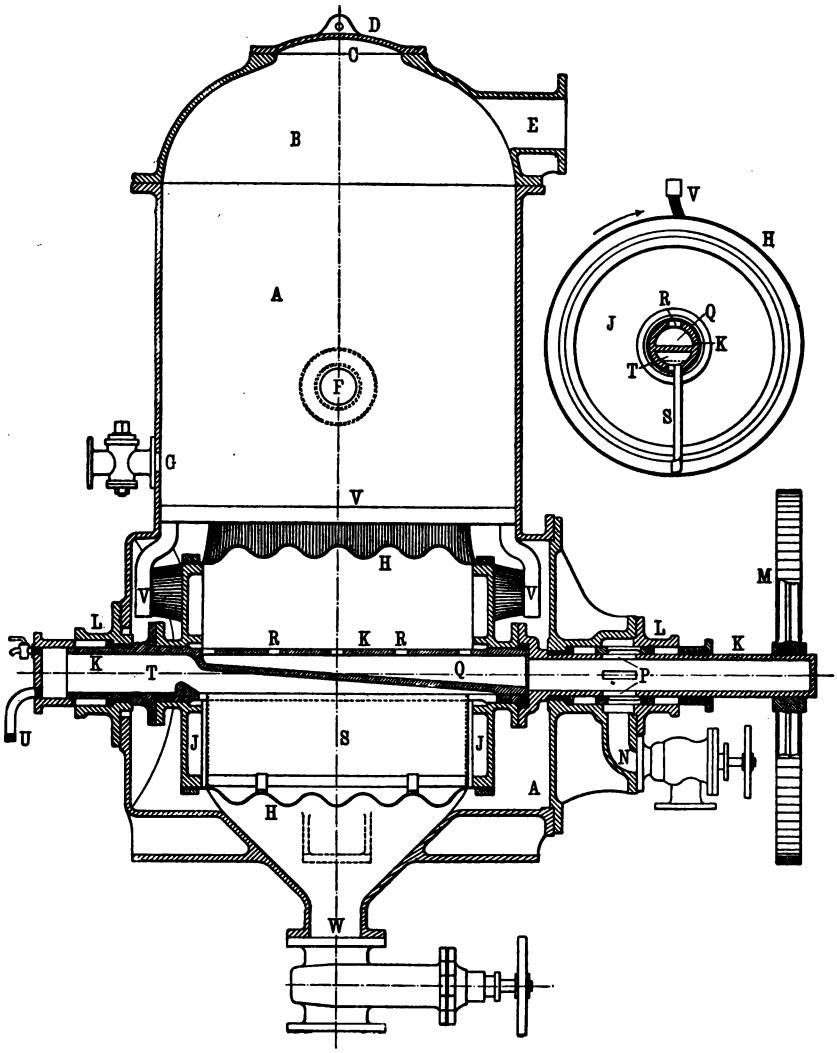
I have repeatedly mentioned the second product obtained in the saponification of oils and fats, viz., glycerin. We have seen that both the soapmaker and the candlemaker recover this valuable by-product. In the case of the candlemaker, the process of recovery is very simple, as the sweet water from the autoclaves works. The outer appearance of a tube evaporater is represented by vessel B in Fig. 28, p. 51.

In the case of the glycerin solutions resulting from the acid-saponification process, large quantities of calcium sulphate remain dissolved. This calcium sulphate separates out on

FIG. 27.



is practically nothing else than a dilute solution of glycerin, which, after some purification, only requires to be concentrated down to a specific gravity of 1·24 (the concentration required by the market). Formerly the apparatus used for the concentration was the Wetzel pan (Fig. 24), but in modern establishments this has been replaced by a vacuum tube evaporator, such as is used in sugar concentrating the solution. Hence a hard crust would be rapidly formed on the tubes, thus very seriously reducing the evaporative power of the apparatus, unless the calcium sulphate were removed continually. In this case, tube evaporators are therefore completely useless, and must be replaced by such apparatus as I shall show have been employed with advantage in the recovery of glycerin from soap lyes.

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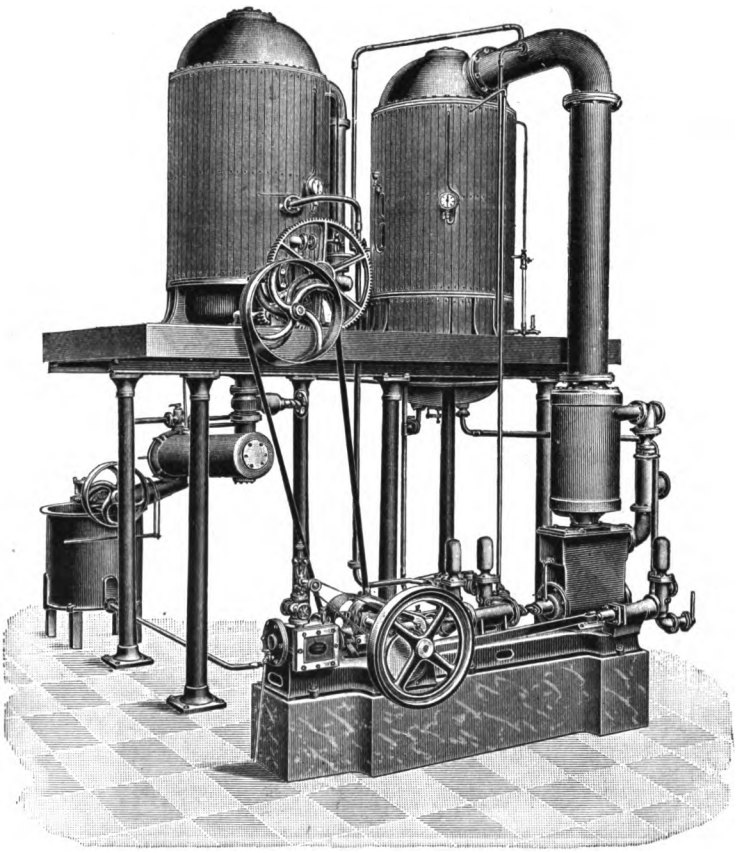
In the case of these lyes the problem is more complicated, inasmuch as we have to deal (after their complete purification) with a solution containing a few per cent. of glycerin only, and a considerable proportion of salt, up to 13 per cent. Now, if the evaporation of these lyes has been carried so far that the proportion of salts reaches about 20 per cent. or more, salt begins to fall out. Since the glycerin has been only enriched so far that its proportion is about 10 to 12 per cent., whilst the finished crude soap glycerin as required by the refiner must contain 80 per cent., it is evident that an enormous amount of salt must fall out, before so high a concentration of the glycerin can be reached. The salt which separates out must of course incrust the vessel in which the concentration is carried out.

When the recovery of glycerin from soap lyes was first introduced, this incrustation caused such enormous trouble that for a long time the new industry was in danger of succumbing to these difficulties. A certain progress was reached through carrying out the concentration in fire-heated pans, the sides of which were kept free from deposit of salt by suitable stirring and scraping arrangements. Later on, evaporation by steam in tube evaporators such as are used in sugar works was introduced; but as these tube evaporators are liable to incrustation with salt and the heating tubes to complete stopping up, I have constructed a (patented) vacuum evaporator, which has been found suitable in practice for the concentration of soap lyes. An evaporator of this type—consisting of one vessel, "Single Effet"—is shown in Fig. 25. Two types of the rotating heating surface are shown in Figs. 26 and 27. From the illustrations it will be gathered that the heating surface is kept clean by means of a mechanical arrangement, so that the salt as it falls down can be drawn off with the help of the vessel attached to the bottom of the pan (Fig. 25), without it being necessary to

FIG. 28.



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interrupt the boiling in the vacuum pan. In large establishments, multiple evaporation commends itself on account of the greater economy. Taking advantage of the fact that up to that point when the salt begins to separate a considerable amount of water may be evaporated without fear of incrustation, I have combined in my (patented) "Double Effet" (Fig. 28), a tube evaporator with the "Single Effet" shown in Fig. 25. The soap lyes are therefore concentrated first in vessel B until they reach "salting point," that is until they reach that point at which the salt commences to separate. They are then transferred into the vessel A, in which the salt is removed as it falls out, whilst the boiling is kept up uninterruptedly. When the specific gravity of the sample has reached 1·3, the finished glycerin is withdrawn. The "Triple Effet" which I show in the next lantern slide is constructed on similar lines.

I exhibit here a number of crude glycerins which have been obtained by the several saponification processes described above.

All these glycerins must be purified by distillation in apparatus similar to that shown in the next slide, in order to be converted into the straw-coloured "dynamite" glycerin of specific gravity 1·261 (various makes of which I show here in these bottles), and by a second distillation into the well-known water-white chemically pure glycerin.

I have endeavoured, in the limited space allotted to me, to lay before you a rapid survey of those industries which, in their aggregate, form the technical side of the fat and oil trade of this country. From the tables of imports and exports given in the first lecture, you have been able to gather the vast extent these industries have reached. Yet not only the amount of capital invested is enormous, but also a very large amount of scientific work has been done in this country in order to place these industries on a thoroughly scientific basis. Here is a branch of chemical industry which proves that this country is in the forefront, and is able to teach our friends on the Continent, and in America, a good deal yet. We are almost daily being confronted by a number of writers with the lament over the backward state of our chemical industries, and the enormous dividends paid by tar-colour manufacturers abroad are being continually held up to us. They all seem, however, to forget the large dividends which our soap and candle manufacturers are paying. Whilst in Germany, as far as I am aware, hardly more than ten or fifteen chemists find employment in the whole soap industry proper, I know of at least two works in this country in which more than that number are engaged. If the high position which the oil and fat industries have earned by hard work, both in the factory and in the laboratory, is kept up by our young men proceeding to work in a truly scientific spirit, then we may rest assured that we shall continue to maintain the supremacy we have held so long in these industries.

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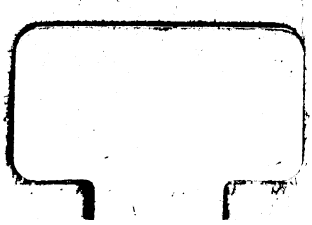

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